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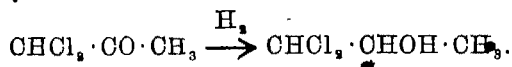
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The Reduction of Unsymmetrical Dichloracetone by Yeast.

BY

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The reduction of chlorinated ketones does not appear to have been studied hitherto, although the reduction of aldehydes and ketones in general by yeast has been the subject of thorough investigation by Neuberg¹ and his co-workers. Their work conclusively proves the value of yeast as a reducing agent, which must play an important part in ordinary fermentation as also in natural syntheses. The first important example of bio-chemical reduction of this nature was furnished by Linter,² Liebig, and Lüers who reduced chloral hydrate and made the preparation of trichlorethyl alcohol accessible in the laboratory. The importance of reducing monochloracetone, or indeed, of any of the unsymmetrical chloracetones by means of yeast, lies firstly in the fact that these acetones after reduction give rise to alcohols containing an asymmetric carbon atom as is evident from the following :



Secondly, these chlorinated secondary alcohols would form the basis of urethane derivatives, valuable as soporifics. In ordinary chemical reduction it is the

¹ C. Neuberg and J. Korb. *Ber* 46, 2225 (1913).

² C. J. Linter and H. J. V. Liebig *H.* 72, 449 (1911); Linter and Luers. *H.* 88, 122 (1913).

racemic form that is invariably obtained, as the chance of formation of the dextro-form is equal to the chance of formation of the laevo-form. In the case of biochemical reduction, the chance of obtaining optically active components is usually great due to the selective action of enzymes, and if in any way the preponderance of one isomer over the other can be secured, the resulting compound should exhibit optical activity (compare Neuberg and Kerb; Neuberg and Nord). An early example of the selective action of ferments or bacteria is to be found in Le Bel's work on the fermentation of inactive propylene glycol by *bacterium termo*. A further example of interest is to be found in the work of Peré,¹ who studied the biochemical oxidation of propylene glycol in contact with *tyrothrix tenuis*. It is significant that this investigator obtained a dextro-rotating propyl glycol, as distinct from the laevo rotatory propyl glycol obtained by Le Bel. The explanation must evidently lie in the use of different bacteria, which would seem to indicate with a degree of certainty that the action of the two bacteria upon racemic propyl glycol is selective.

The particular reaction described in these pages is a case of reduction by yeast in a fermenting solution of sugar. Here also the yeast exerts a selective action and from unsymmetrical dichloracetone gives rise to an optically active dichlorisopropyl alcohol. The rate of this reduction, however, in the case of dichloracetone is relatively rapid as the reduction is probably completed in 24 hours if not in 12 hours. The operation of adding a 20 per cent. alcoholic solution of 10 grams dichloracetone to a fermenting solution of sugar requires 3-4 hours, after which the mixture is allowed to stand

¹ Annales de l'Institut Pasteur, 1896, II, 600-8.

overnight in an incubator at 35°C. Next morning the odour of dichloracetone is scarcely to be noticed in the reaction mixture, and the sugar is also found to have disappeared to the extent of 96-97 per cent. The further addition of yeast, or of yeast and sugar, is only to secure certainty of reduction of any dichloracetone that might have remained unacted upon. Dichloracetone does not seem to be appreciably poisonous to beer-yeast and the yield of dichlorisopropyl alcohol is not affected by the rate of addition of the dichloracetone to the fermenting sugar solution. In one experiment in which accidentally the stopper of the dropping funnel was dislodged, about half of the alcoholic solution of dichloracetone fell at once into the fermenting sugar solution without markedly affecting the rate of fermentation of the solution. This non-poisonous character of dichloracetone is convenient and also interesting in view of the fact that Willstätter has recently found bromal very poisonous to yeast and Neuberg (*loc. cit.*) found it necessary to add the aldehydes with which he experimented, very cautiously to the fermenting solution in order to get a good yield of reduction product. Also in some experiments with monochloracetone the rate of addition was found to be very important. The first experiment was conducted with monochloracetone supplied by Messrs. Kahlbaum of Berlin, an alcoholic solution of which had to be very cautiously added in order to maintain the fermentation of the sugar solution. In fact even with the utmost care, it was difficult to maintain a brisk fermentation throughout the addition, and towards the end the addition of monochloracetone had actually to be suspended, in view of the considerably decreased rate of fermentation. It is to be observed here that in course of further investigation, it was found that the monochloracetone supplied by Messrs.

Kahlbaum was not pure, but contained a considerably higher percentage of chlorine than is required by the formula. This may be due either to the presence of some dichloracetone, the boiling point of which closely approaches that of monochloracetone, or to small quantities of higher chlorinated products. The conclusion, therefore, is that either monochloracetone or the very small quantities of tri-, tetra-, or penta-, chlor derivative of acetone, are poisonous towards yeast, dichloracetone itself having scarcely any injurious effect. Experiments with monochloracetone alone could not be completed on account of the difficulty in obtaining a pure specimen of the substance. Its preparation has now been undertaken. In the case of monochloracetone something different occurs, as the peculiar penetrating odour of this compound remains for over a week, and indeed does not then entirely disappear. In our experiments we followed the conversion of monochloracetone into monochlorisopropyl alcohol by the disappearance of this unpleasant and tear-bringing odour. As already mentioned, the poisonous nature of monochloracetone or any component with which it is contaminated, is so marked that a little carelessness in the addition of its alcoholic solution to the fermenting sugar solution speedily stops the fermentation. It is significant that monochloracetone has a fatal action upon yeast, whereas dichloracetone has practically no such injurious action. A careful comparison of the various chloracetones with regard to their action on yeast would be of interest and it is hoped that a future communication may be made thereon.

Whilst in the cases cited above (Neuberg, Pere, Le Bel) the rotation in two experiments was not constant, with dichloracetone however, this has been found to be the same in five separate experiments that have up to now been performed.

An additional interest in obtaining unsymmetrical dichlorisopropyl alcohol by the biochemical method lies in the ease with which a good and cheap yield of this alcohol can be obtained, rendering the process thereby suitable for practical application.

Several experiments have up till now been performed both with the alcohol itself and its urethane derivative, upon rabbits, which justify the expectation that they will be valuable as soporifics. It is to be observed that dichlorisopropyl alcohol is likely to have an advantage over chloral, being poorer in chlorine, and more effective than trichlor ethyl alcohol, being a secondary alcohol. All experiments, that as yet it has been possible to conduct, show that both the alcohol and the urethane derivative are without any injurious effect upon the animal system, and that the difference between the narcotic and toxic doses is fairly considerable. A more detailed report of the investigation in this direction will be shortly communicated.

EXPERIMENTAL.

250 grams of starch sugar or ordinary cane sugar were dissolved in 2.5 litres of tap water at 40° in a 5 litre bottle. To the solution 250 grams of pressed beer-yeast were added. In about fifteen minutes the liquid was in brisk fermentation, when a 25 per cent. alcoholic solution of 10 grams dichloracetone was drop by drop added to the fermenting mixture, care being taken not to suppress the vigorous fermentation by too quick addition of the dichloracetone solution. In three to four hours the addition is complete, during which time the bottle is shaken from time to time. The reaction vessel is then allowed to stand over-night in an incubator at 35°C. Next morning the odour of dichloracetone

is found to have practically disappeared, and the sugar also almost fully used up. In order to ensure more complete reduction, about 100 grams more yeast are added and left again in the incubator for two more days, at the end of which the liquid is filtered, the residue washed two or three times and the combined filtrate distilled under vacuum on a boiling water-bath. The ethyl alcohol, dichlorisopropyl alcohol and any unchanged dichloracetone being volatile in steam, collect in the receiver which is constantly kept well-cooled by a rapid current of tap water. The distillate is now shaken up with two litres of ether, the ethereal layer separated, dried over ignited sodium sulphate, and distilled off from a water bath. The residue which now amounts to 8 cc. is fractionated from a small distilling flask, when 5.2 grams of dichlorisopropyl alcohol collect steadily at 146° - 148° [compare Wohl and Roth, Ber. 40, 217 (1907)]. The fore-fraction also contains about a gram of the dichlorisopropyl alcohol identified by its optical rotation. From a large scale experiment with 48 grams of dichloracetone, 26 grams of the pure alcohol were obtained, which correspond to a yield of 54 per cent. of the theory.

Dichlorisopropyl alcohol is moderately soluble in water and very soluble in ether and alcohol. It has a burning sweet taste, and a pleasant ethereal odour, having a density of 1.33. The pure liquid in a one decimeter tube rotates the plane of polarisation by -11.88° . $[\alpha]_D$ is therefore -9° .

Found C=27.83, H=4.76, Cl=54.0; $C_3H_5OCl_2$, requires

C=27.91, H=4.65, Cl=55.0 per cent.

The urethane derivative $\begin{array}{c} \text{OH} \\ | \\ \text{CHCl} \cdot \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \end{array}$ is prepared by mixing an ethereal solution of carbamyl chloride

with the calculated quantity of dichlorisopropyl alcohol also in ethereal solution. The solution is allowed to stand at room temperature for 15 minutes, after which the ether is expelled on the water-bath. The residual oil soon solidifies on scratching with a glass rod and can then be crystallised either from ether in which it is extremely soluble, or from water in which it is soluble only to the extent of 2 per cent. at ordinary temperature. This is a decided advantage as the loss in crystallising from ether is excessive. The urethane crystallises in white needles, melting at 61° - 63° C.

0.1330 gave $N=9.4$ cc., at 16° C and 755 mm. press ; $N=8.20$; $C_4H_7O_2NCl_2$ requires $N=8.14$ per cent. 0.75 gram of the urethane dissolved in 25 cc. of water and 2 cc. of glycerine when given to a rabbit weighing 4.5 pounds caused an uninterrupted sleep for 11 hours. The parent alcohol given in 0.5 gram caused an undisturbed sleep in the same animal for a period of one hour, without spasms. The urethane derivative is also optically active, rotating the plane of polarisation to the left. 0.3336 gram dissolved in 2 cc. of absolute alcohol, rotated the plane through -2.226° in a 1 dm. tube. The reduction of monochloracetone (from Kahlbaum) by a method similar to that adopted in the case of dichloracetone, resulted in a yield of not more than 25 per cent. In fractionating the final product of reduction after extraction with ether, the first part of the distillate, after expulsion of the ether distilled under 100° C and contained mostly ethyl alcohol ; the fraction distilling between 100° and 125° contained unconverted monochloracetone and also a small quantity of monochlorisopropyl alcohol, $CH_2Cl.CH(OH).CH_3$, the boiling point of which latter is 127° . Then came a fraction boiling between 126° and 132° which may be taken as more or less pure monochlorisopropyl alcohol, but the thermometer then rose rapidly, a product boiling

Between 138° and 152° was collected which probably marks the boiling point limits of a mixture of mono- and dichlorisopropyl alcohol. After this the thermometer rose steadily up to 180° and a few drops of liquid of unknown composition were obtained.

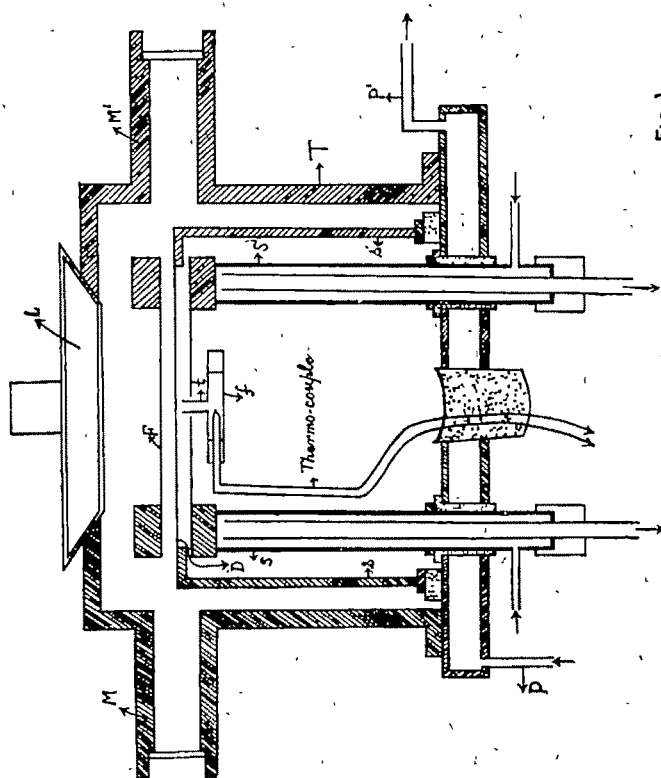


Fig. 1

On An Experimental Test of Thermal Ionisation of Elements.

BY

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Though the theory of thermal ionisation of gases has been given by one of the authors in a number of papers¹ about three years ago, its application has hitherto been confined mostly to the realm of astrophysics. The theory still lacks experimental confirmation in the laboratory, and the present communication is the outcome of an attempt just to remove this desideratum.

The underlying idea may be thus stated :—

If we take any element in the vapour state, and go on heating it, its electrical and optical properties will undergo a gradual change. To visualize matters, let us start with Ca-vapour at 800°C. At such a low temperature, it is most probably a non-conductor of electricity and will show only the lines $\lambda=4227$, 1S-2P, $\lambda=6573$, 1S-2p₂ and other lines of the principal series in absorption. If we go on heating the gas, a stage will come when an appreciable fraction will be ionised. The vapour space will now conduct electricity, and will show the principal lines of Ca⁺, $\lambda=3968$ (H), and $\lambda=3933$ (K) in absorption. Between these two stages, the lines of subordinate series of Ca may also come out in absorption.

For sometime past, one of the authors has been trying to follow this process in the laboratory. The first attempt

¹ Proc., Roy. Soc. Lond., Vol. 99, p. 136, et. seq. Zs. f. Physik, Vol. 6, p. 40.

was made with the vapours of the alkali metals, because as these elements possess the lowest ionisation-potentials, it was expected that they would be copiously ionised even at such low temperatures as 800°C — 1000°C . But it may be mentioned here that these metals are not suitable for the spectroscopic test, as their chief ionised lines lie far down in the ultraviolet.

The experiments on the electrical conductivity of heated alkali vapours were first undertaken at the laboratory of Prof. Nernst at Berlin, and the preliminary results which we obtained quite confirmed our expectations. It was found that Cs-vapour¹ at 1250°C possessed an enormous specific conductivity of $(50\text{ ohm})^{-1}$, which diminished gradually as the temperature was lowered, and at 850°C , was certainly smaller than $(10000\text{ ohm})^{-1}$. It was also found that the specific electrical conductivities were in the order $\text{Cs} > \text{R} > \text{K} > \text{Na}$, just as their ionisation-potentials would lead us to expect.

The furnace in which these experiments were carried out was not suitable for combined electrical and optical investigation as described above. Moreover, according to theory, the fraction of atoms ionised is a function of not only the temperature, but also of pressure. Hence it is desirable that a furnace be designed in which both temperature and concentration can be varied at will. In Nernst's furnace, pressure could not be varied at all.

In order to remove these defects, another arrangement was devised, which is described below.

This consists of two furnaces in vacuum. The material which is experimented upon is placed within the

¹ Lewis reports in his *Thermodynamics* (p. 460) that Urey carried out at his suggestion a similar experiment on the electrical conductivity of heated Cs-vapour. The full details of the paper are not yet available. The experiment mentioned above is fully described in the *Journ. Dept. of Science*, 1922, Calcutta University.

small furnace, which is heated to a varying temperature. The vapour pressure of the substance is known from this temperature. The substance in the vapour form is led to the bigger furnace which is maintained at a higher temperature. The volume within the big furnace containing heated vapour forms the experimental space, of which the electrical and spectral properties are studied. The great advantage in this type of furnace is that they allow both the temperature and concentration to be varied at will, which is not possible in the type used by A. S. King in the Mount Wilson Solar Observatory.

THE FURNACE.

The furnace is shown diagrammatically in fig. 1. It is simply an adaptation of Prof. Compton's furnace (described in the Journ. Opt. Soc. America, Oct., 1922), with some modification to suit our convenience.

B=A rectangular hollow brass base, made of thick sheets of brass cooled by water, by inlet and outlet pipes at P and P¹.

T=Heavy box of cast iron in the form of a rectangular parallelopiped, open at the bottom, and provided with flanges on all sides at the bottom for air-tight contact with the brass base. The joint was kept airtight by a preparation of resin and bee's wax.

M, M¹=Projecting tubular pieces, of one piece with the box, and closed by glass or quartz plates, which are cemented to it by means of shellac.

L=Removable circular lid with a ground conical periphery and fitting into a ground, and sloping circular opening on the top of T. By taking out L, easy readjustments could be quickly made in the interior. This was just to avoid taking off the whole box T after every experiment for the necessary readjustments. The two

surfaces of contact were ground with great care till they fitted exactly into each other.

F=Furnace which in the preliminary experiments consisted of a sheet of iron rolled into the form of a circular tube. It was clamped by means of a headpiece and screws on the water-cooled stands,—S and S' which consist of thick iron tubes with a rectangular top of solid iron. The stands were water-cooled as shown in the diagram. The surface of the sheets was cleaned by the pickling process used in enamelling and then smoothed by emery paper.

D=A thick wire of iron, clamped on the stand 's' at one end and sliding in a groove at the head of the stand s' at the other end.

About half the space inside the furnace F was clear.

A current of 500-1000 amperes was applied to F under 6-10 volts directly from a battery of accumulators with a sliding resistance of mercury. Owing to the large size of the furnace, and the limited energy supply at our disposal, the temperature could not be raised higher than 1250°C , as eye observations would indicate. A low tension transformer as used by King would have been much better, but as we had not the means to buy one, we had to make the best use of a set of discarded storage cells. One great disadvantage was that after about 5 minutes the connecting wires became very hot, and less current flowed through F, and temperature rapidly fell. This defect would probably be cured if the furnace could be heated by current from a low-tension transformer, with very short and water-cooled leads. The furnace was evacuated by a Gaede oil pump, which was kept continuously running during the experiment. The leak was so small, that even at a temperature of 1250° , iron did not appreciably oxidise though the experiment lasted from 5-10 minutes.

f = Another furnace of much smaller dimensions, heated directly by current from accumulators, the substance which was to be vaporised was kept inside the furnace here. The ends were blocked by iron-plugs, through one of which passed a thermo couple of iron and constantan shielded by pyrex glass tubing.

t = Small porcelain tubing, leading the vapour through an orifice at the top of f to the heated space inside F .

The connections to f for leading the heating current consisted of thick copper rods (not shown in the diagram) passing through an India rubber cork, which closed an orifice at B . The leads for thermo couple were also taken through this cork.

The temperature to which f was heated could be obtained from the readings on the millivoltmeter to which the couple was connected. Then from the data on the variation of vapour pressure with temperature, the pressure in f could be obtained. The pressure in F is equal to that in f , if the free flow could be prevented by stopping the ends of F by quartz plates. This has not yet been attempted.

By this arrangement, it was hoped that the vapour of any element could be maintained at a definite pressure for any length of time. Experimental difficulties have, however, not been completely overcome, but the progress hitherto made has been sufficient to justify the expectations placed in this arrangement.

DESCRIPTION OF THE ARRANGEMENT FOR MEASURING THE ELECTRICAL CONDUCTIVITY.

The arrangement for measuring the electrical conductivity is shown in diagram No. 2.

B — Battery.

V — Voltmeter for measuring the potential difference between the central wire and the furnace.

F—Furnace.

R—Resistance for varying the voltage.

K_1 K_2 —Two three-way keys.

M. A—is a milliamperemeter placed between one set of knobs of K_1 and K_2 .

Mic. A—is a microamperemeter placed between another set of knobs.

G—is a sensitive galvanometer placed between another set of knobs, with a variable megohm in series. By manipulating the keys K_1 , K_2 , the furnace may be connected either through the milliammeter, the microammeter or the galvanometer. Voltage divided by the current gives the resistance of the vapour-space in the furnace.

ACTUAL EXPERIMENT.

The results which are communicated here are only of a preliminary nature.

The actual procedure was as follows :

Firstly, the central furnace was heated, and the thermionic current between the furnace and the central wire was measured. In most cases, this could be done by means of the galvanometer.¹ The thermionic current is a very good indication of the temperature of the furnace F. Then current was applied to the small

¹ It will be interesting in this connection to recall the experiments of Pring and Parker who investigated the thermionic emission from large carbon rods by heating them with the aid of very large currents. They found that with larger currents thermionic emission died down. Richardson pointed out that this was due to the large magnetic field of the heating current, which prevented the electrons to escape from the heated surface. In our experiment, though we are using currents of the order of 10^3 Amp, the experiment is being performed *inside* the heated space, where the magnetic field is zero, so that there is free thermionic emission. Incidentally, it may be mentioned that in this method the temperature of the emitting surface can be more precisely measured, if we direct the optical pyrometer to the interior, for radiation coming from inside the furnace approximates to the black body condition. The point is receiving attention.

furnace *f*. The substance vaporised, and the vapour passed into F. Then the observer at the galvanometer noted whether the spot of light in the galvanometer scale shifted its position. Simultaneously, another observer noted the readings on the millivoltmeter connected with the thermocouple.

If the spot of light went off the scale, the galvanometer circuit was shunted off, and the microammeter circuit was put in, and the current observed. If this did not suffice, the milliammeter circuit was inserted.

The pump was kept running during the whole course of the experiment, which generally took from 5 to 10 minutes.

When experiment with one substance was finished, and the furnace cooled down the lid was taken off. Then the small furnace *f* was replaced by a fresh one, because the old furnace is generally contaminated by deposits of the metal with which the previous work has been done. The big furnace F was replaced, only if it was broken, as frequently happened, probably owing to stress developed during expansion.

Series 1. Experiments with Hg, Cd and Zn.

These three metals are interesting, because the electrical conductivity of their vapours in a flame were investigated by McLennan¹ a few years ago. The electrical conductivity of heated mercury vapour has formed the subject of investigation by many workers including Maxwell, Hittorff, J. J. Thomson and Strutt, but the results were mutually contradictory. McLennan's results also were quite indecisive.

We have proved decisively that when vapours of these elements are introduced into the furnace, between

¹ Proc. Roy. Soc., Lond., Vol. 92, p. 592.

the temperature 850°C to 1300°C , the thermionic current remains completely unaltered. The voltage applied was 1.34, and at the highest temperature employed by us (1300° as judged by visual observation), the thermionic emission was 10 microamperes, with $R=9000$ ohm in series. The temperature of the small furnace was 650°C , corresponding to a vapour pressure of 27.23 mm. of Zn. It was found that when Zn-vapour was evolved, there was not only no increment in the thermionic current but there was actually a slight falling off, owing probably to the cooling of the furnace by the passing Zn vapour. The same phenomena was observed with Hg and Cd, the last being operated at a temperature of 740°C , vapour pressure = 557.2 mms. of mercury.¹

These experiments prove conclusively that vapours of Zn, Cd, and Hg are not ionised at all by heat up to temperatures of 1250°C . This is quite expected as the ionisation-potential of these elements are rather high, viz., 9.45, 9.40, 10.45 volts.

Experiments with Mg and Ca.

Magnesium.—The small furnace was heated to 750° (measured), and the large furnace to about 1300°C (not measured). The thermionic current was 10×10^{-8} amperes. On putting Mg-vapour, the current rose to $\frac{2}{10}$ of a milliampere, or 200×10^{-8} Amp. or by about 20 times, so that magnesium vapour seems to have been ionised at 1300°C .

Calcium.—The small furnace was maintained at 920°C (measured), but the storage cells having run down, the temperature in the big furnace F could not be increased. It was probably 1150°C . The thermionic emission was less than a microampere, but on putting

¹ These figures are taken from Landolt and Bornstein's tables, 6th edition, pp. 1332-1338.

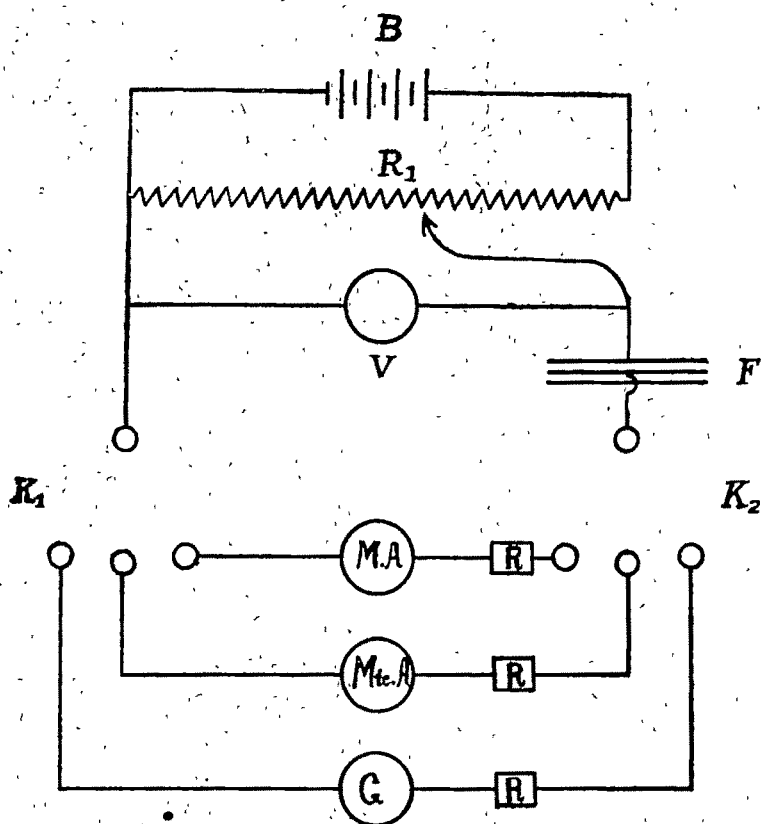
Connections

FIG. 2

Ca-vapour, it rose to 30 microamperes. This proves that Ca-vapour is appreciably ionised at 1100°C.

Sodium.

Sodium.—The small furnace was maintained at 470°C, corresponding to a vapour pressure of about 2 mm. of mercury. The temperature in the big furnace was about 900°C. The thermionic emission amounted to 40 divisions on the galvanometer scale corresponding to a total resistance 5×10^8 ohms. As one megohm was put in the galvanometer circuit, the resistance of the furnace-cell was approximately 4×10^8 ohms. On putting Na-vapour the spot went off the scale at once, so that the micro-ampere circuit was put in. Even this went off the scale. Then the milliamperemeter circuit was put in with no resistance in series. The current was $\frac{1}{10}$ of a milliamperere, so that the equivalent resistance with Na-vapour was only 13400 ohms. Thus at 900°C the conductivity of the space increases about three hundred times, when Na-vapour is put in.

The only objection which can be raised against the view that Na or Ca-vapour is ionised by heat is that the electrons emitted from the surface of the furnace F in falling to the central wire, produce fresh ions by collision. This possibility is excluded by the fact that the potential difference between the furnace and the central wire is only 1.34 volt, much lower than the ionisation potential of the elements investigated. But it may be contended that since the total potential fall between two ends of the furnace is from 6 to 10 volts, electrons emitted from the negative end may just slip along the surface and come out at the end with an energy corresponding to a voltage drop of 6 to 10.

Though we can think of such an eventuality the probability of its affecting the main results seem to be

rather remote. At least, in future experiments, efforts will be made to free the arrangement from the possibility of such an objection.

In conclusion, we wish to record our thanks to our colleague Mr. S. Bhargava, Reader in this University, for useful help in designing the apparatus and to Mr. K. Majumdar, Research Scholar, for help in taking observations.

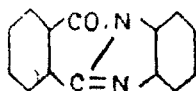
The Colour of Complex Diazoles.

Part I.

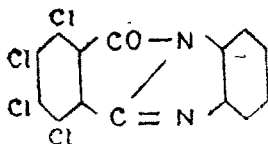
BY

GOPÁL CHANDRA CHAKRAVARTI.

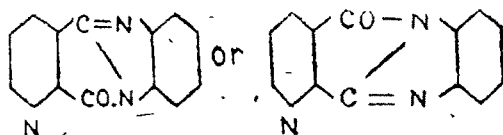
1:2-Orthobenzoylene-1:3-benzdiazole is obtained in a good yield by the fusion together of phthalic anhydride and o-phenylene diamine (Bistrzycki and Lecco, *Helv. Chim. Acta.*, 1921, 4, 425; compare also Thiele and Falk, *Annalen*, 1906, 347, 112; and Rupe and Thiess, *Ber.*, 1909, 42, 4287). Bistrzycki and Lecco (*loc. cit.*) applied the same method to the condensation of o-phenylene diamine with tetrachlorophthalic acid, and with quinolinic acid. 1:2-o-Benzoylene-1:3-benzdiazole



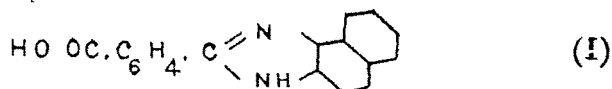
has been recognised to be a powerful chromophore and contains a fused pyrrol-iminazole ring in its skeleton. Both the diazoles, tetrachloro-1:2-o-benzoylene-1:3-benzdiazole,



and 1:2-(α,β)-picolinoylene-1:3-benzdiazole,



contain the fused pyrrol-iminazole ring systems but whereas the former is coloured greenish-yellow the latter is absolutely colourless. This absence of colour in the picolinoylene compound may be due to the strong hypsochromic character of the pyridyl nitrogen atom (compare Ghosh, T., 1919, 115, 1103) which neutralises the chromophoric nature of the pyrrol-iminazole system. These important chromogenic properties of the fused heterocyclic system led the present author to investigate the properties of a series of analogous compounds which contained the pyridine-iminazole skeleton. With this view, as also with the object of studying the influence of additional fused ring systems on the depth of colour of these compounds, intermediates already containing fused rings such as 1:8-naphthalic anhydride and 1:2-naphthylene diamine have been employed in the condensation. Phthalic anhydride combines with 1:2-naphthylene diamine in alcoholic solution (compare Hans Lieb, Monatsh, 1918, 39, 873), to form 1':2'-naphthiminazole-2-phenyl-o-carboxylic acid,



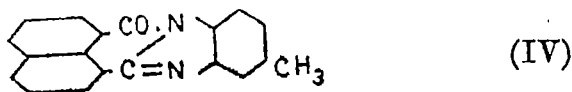
which on treatment with acetic anhydride or on being heated to a high temperature loses a molecule of water and is converted into 1:2-o-benzoylene-1:3-naphthadiazole,



The latter crystallises in beautiful orange-yellow prisms. 1:2-(1':8')-Naphthoylene-1 3:-benzdiazole,



derived from naphthalic anhydride and o-phenylene diamine has an intense yellow colour. 1:2-(1':8')-Naphthoylene-1:3-(-2'') methylbenzdiazole

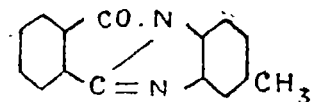


obtained from naphthalic anhydride and orthotoluylene diamine is coloured deeply yellow. The colour of 1:2-(1':8')-naphthoylene-1:3-(1'':2'')-naphthiminazole



obtained by the condensation of naphthalic anhydride with 1:2-naphthylene diamine is orange-red. All the compounds with formulæ III, IV and V contain a pyridine ring fused with an iminazole, one and all of them are intensely coloured. Thus like condensed pyrrol-iminazole ring systems, the pyridine-iminazoles also possess marked chromophoric properties. This is also borne out by the experiments of Bistrzycki and Fässler (Helv. Chim. Acta., 1923, 6, 519) who find that the compound obtained by the condensation of homophthalic anhydride with o-phenylene diamine is coloured.

1:2-Orthobenzoylene-1:3-(2')-methyl-benzdiazole



obtained by the condensation of phthalic anhydride with 1:3:4-o-toluylene diamine is found to resemble 1:2-o-benzoylene-1:3-benzdiazole in colour. It thus appears that the effect of the presence of increasing fused ring systems is to deepen colour and that the naphthiminazoles

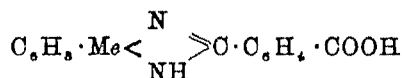
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are generally more strongly coloured than the benzimidazoles. A comparison of colour of these compounds will make the point clear.

1 : 2-orthobenzoylene-1 : 3-benzdiazole	...	Yellow.
1 : 2-orthobenzoylene-1 : 3-methylbenzdiazole	...	Do.
1 : 2-o-benzoylene-1 : 3-naphthadiazole	...	Orange-yellow.
$\alpha\beta$ -diphenylacrylenebenziminazole	...	Brown.
(Bistrzycki and Fässler, <i>loc. cit.</i>)		
O-phenyleneacetyl-2 : 1-benzimidazole	...	Yellow.
(Bistrzycki and Fässler, <i>loc. cit.</i>)		
Tetrachloro-1 : 2-o-benzoylene-1 : 3-benzdiazole	...	Greenish-yellow.
(Bistrzycki and Lecco)		
1 : 2-(1' : 8')-naphthoylene-1 : 3-benzdiazole	...	Deep yellow.
1 : 2-(1' : 8')-naphthoylene-1 : 3-methyl-benzdiazole	...	Do.
1 : 2-(1' : 8')-naphthoylene-1 : 3-naphthiminazole	...	Orange-red.

EXPERIMENTAL.

Condensation of Phthalic Anhydride with 1 : 3 : 4-o-Tolylene Diamine. The Formation of Tolyleneamidine-benzenyl-o-carboxylic acid.—



Identical with the compound obtained by Bistrzycki (B. 23, 1042-1046) by the treatment of o-tolylene diamine with phthalaldehydic acid, is prepared by mixing together 3 gms. of the anhydride, 2.6 gms. of the diamine and 40 c.c. of absolute alcohol. The mixture is refluxed on the water bath for nearly 3 hours and allowed to cool. The residue is filtered off, washed with a little alcohol and ether and crystallised from 50% acetic acid. It has the melting point 260-262°. It is insoluble in water, chloroform, acetone, ether and toluene. It dissolves fairly in

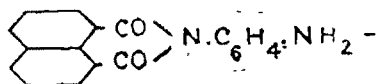
mineral acids and also in alkalies and alkaline carbonates. (Found: C=71.18; H=4.51. $C_{15}H_{13}N_2O_2$ requires C=71.43; H=4.76 per cent.).

1:2-Orthobenzoylene-1:3-methylbenzodiazole (VI).—

The amidine carboxylic acid described above is heated in a dry tube when the diazole partly sublimes and condenses on the cooler part of the tube. This is scraped off and crystallised from absolute alcohol. The crystals are yellow and melt at 166°. They dissolve in concentrated sulphuric acid giving a yellow solution with a green tint. (Found: C=76.75; H=4.50. $C_{15}H_{10}N_2O$ requires C=76.92; H=4.27 per cent.).

*1':2'-Naphthimīnazole-2-phenylorthocarboxylic Acid (I).—*Lieb (*loc. cit.*) obtained this compound as a by-product during the preparation of diphtalyl-1:2-naphthylene diamine. But by boiling an absolute alcoholic solution of phthalic anhydride and 1:2-naphthylene diamine in equimolecular quantities for three to four hours, nearly a quantitative yield of the acid is obtained. The product of the reaction is cooled, the precipitate filtered off and repeatedly extracted with hot alcohol and acetone. The residue is then finally crystallised from nitrobenzene. The crystals melt above 300°. (Found: C=75.21; H=4.30. $C_{18}H_{12}N_2O_2$ requires C=75.00; H=4.16 per cent.).

Condensation of Naphthalic Anhydride with Orthophenylene diamine—the Formation of Orthoaminonaphthalanil:—



Three grams of the diamine are dissolved in 60 c.c. of absolute alcohol and five grams of naphthalic anhydride are then added to it. The mixture is then boiled under

reflux for 6—8 hours. On cooling the precipitate is filtered off and crystallised from acetone. The product is treated with sodium carbonate solution. The undissolved residue washed with hot water, melts at about 245° with decomposition with previous softening. (Found : $C=74.92$; $H=4.25$; $N=9.57$. $C_{18}H_{12}N_2O_2$ requires $C=75.00$; $H=4.16$; and $N=9.72$ per cent.). The alkaline extract on acidification with concentrated hydrochloric acid yields silky needles of benziminazole-2-naphthyl-8'-carboxylic acid melting at $265-269^{\circ}$.* (Found : $N=9.61$. $C_{18}H_{12}N_2O_2$ requires $N=9.72$ per cent.).

Acetyl Derivative.—The orthoaminonaphthalanil is dissolved in pyridine, acetyl chloride is added to it drop by drop and the mixture allowed to stand for about half an hour. On pouring the liquid into water and stirring with a glass rod the acetyl derivative solidifies. It is then crystallised from glacial acetic acid. It has the melting point 224° . (Found : $C=72.50$; $H=4.63$. $C_{20}H_{14}N_2O_2$ requires $C=72.72$; $H=4.24$ per cent.).

Benzoyl Derivative.—The orthoaminonaphthalanil is dissolved in pyridine and drop by drop an excess of benzoyl chloride added to the solution. It is allowed to stand for 10 minutes and a small quantity of hot water is added to it. The benzoyl derivative which crystallises out in yellow needles is recrystallised from pyridine and water. It melts at 209° . (Found : $C=72.86$; $H=4.52$; $C_{25}H_{18}N_2O_4$ requires $C=73.17$; $H=4.40$ per cent.).

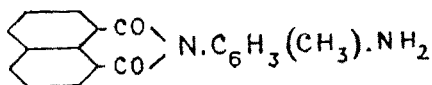
N-Ethyl Derivative.—The orthoaminonaphthalanil is heated under reflux with excess of ethyl iodide for 6—8 hours. Then the excess of ethyl iodide is evaporated off and the product crystallised from alcohol. It melts at $235-37^{\circ}$. (Found : $C=75.69$; $H=5.36$. $C_{20}H_{16}N_2O_2$ requires $C=75.95$; $H=5.06$ per cent.).

* All these compounds on heating are transformed into the corresponding diazoles. He melting points often are found to be not very sharp.

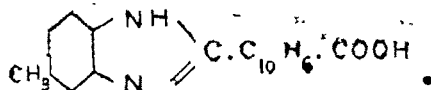
1:2-(1':8')-Naphthoylene-1:3-benzdiazole (III).—

The orthoaminonaphthalanil or the benziminazole-2-naphthyl-8'-carboxylic acid is heated at a temperature of 210—220° in an oil bath for about 2—3 hours. The substance gradually softens and finally becomes liquid. It is allowed to cool and extracted with absolute alcohol from which medium the diazole crystallises in deep yellow needles m. p. 198°. (Found: C=79.93; H=3.88. $C_{18}H_{10}N_2O$ requires C=80.00; H=3.70 per cent.). The same change occurs if either the anilide or the acid be boiled with acetic anhydride.

Condensation of Naphthalic Anhydride with Orthotoluylene Diamine.—4 gms. of naphthalic anhydride are mixed with 2.6 gms. of orthotoluylene diamine and 50 c.c. of absolute alcohol. The mixture is boiled on the water-bath for 6 hours. After allowing to cool the precipitate is filtered off and washed with a little alcohol. It is then extracted with boiling xylene. The xylene solution shows intense green fluorescence and on cooling deposits bright yellow crystals of orthoaminotolynaphthalimide,



m. p. 196°. (Found: C=75.31; H=4.52. $C_{19}H_{14}N_2O_2$ requires C=75.50; H=4.63 per cent.).

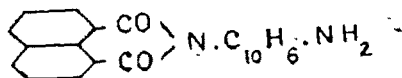
Toliminazole-2(1')-naphthyl-8'-carboxylic Acid,

The residue after extraction with xylene in the above experiment is dissolved in alkali, filtered and the solution neutralised with hydrochloric acid. The colourless crystalline product is filtered off, washed with water and dried. It melts at 273—75°. (Found: C=75.58; H=4.81. $C_{19}H_{14}N_2O_2$ requires C=75.50; H=4.63 per cent.).

I: 2-(1': 8')-Naphthoylene-1: 3-methylbenzodiazole (IV).

—When the o-aminotolynaphthalimide is heated in a tube a deep yellow product boils over and condenses in the cooler part of the tube. The latter is crystallised from alcohol into deep yellow needles m. p. 187°. (Found: C=80.11; H=4.60. $C_{19}H_{12}N_2O$ requires C=80.28; H=4.22 per cent.).

Condensation of Naphthalic Anhydride and 1: 2-Naphthylene Diamine—the Formation of 2'-Amino-N-(1')-naphthyl-naphthalimide.—



Equimolecular quantities of the anhydride and the diamine are mixed with absolute alcohol and boiled for 10–12 hours. The brown precipitate is filtered off and extracted with alcohol, acetone and carbon bisulphide. The residue is finally crystallised from nitrobenzene. M. p. above 300°. (Found: C=77.79; H=3.98. $C_{22}H_{14}N_2O_2$ requires C=78.10; H=4.14 per cent.).

*1: 2-(1': 8')-Naphthoylene-1: 3-naphthiminazole (V).—*The naphthalimide described above distills over on heating. The solid product is extracted with absolute alcohol which on cooling deposits beautiful orange-red crystals m. p. 256°. It dissolves in concentrated sulphuric acid giving an yellow solution with intense green tint. (Found: C=82.24; H=4.51. $C_{22}H_{12}N_2O$ requires C=82.50; H=4.37 per cent.).

Further investigation to establish a relation between the colour and constitution of the diazoles is being carried on.

In conclusion, the author's best thanks are due to Sir P. C. Ray for his kind interest and encouragement during the progress of the investigation.

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Interaction of Sulphur Monochloride with Organic Acid Amides.

Part II

BY

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AND

CHATURBHAI SHANKARBHAI PATEL.

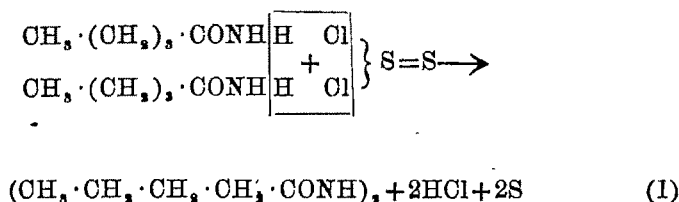
It is well-known that dry gaseous ammonia interacts vigorously with sulphur monochloride with the precipitation of sulphur (Naik, T., 1921, 119, 1166). In a previous communication (*loc. cit.*), it was shown that when this ammoniacal reactivity was neutralised by strong acid residues, *e.g.*, in the organic acid amides such as oxamide, malonamide, succinamide, phthalamide, etc., sulphur monochloride reacts no longer. Between these two extreme limits, of vigorous reactivity and no reactivity, come a number of cases where the reactivity of the amido group is only partially neutralised by the acid character of other residue.

The amides of acetic and benzoic acids interact with sulphur monochloride giving a mono-sulphide (*loc. cit.*), which is presumably derived from a disulphide, $\left. \begin{array}{c} -\text{NH} \\ -\text{NH} \end{array} \right\} \text{S}=\text{S}$, that had been initially formed.

The work described in this paper was undertaken with a view to throw some additional light on the conditions governing the reactivity of the amido group in organic

acid amides, and also on those which govern the stability of the sulphur atom present in the resulting monosulphides. By weakening the acid residue of the amides still further, the reactivity of the amido group may be slowly increased, a point being ultimately reached where it is possible that the monosulphide would change into a condensed di-imido or hydrazine, $\begin{array}{c} -\text{NH} \\ | \\ -\text{NH} \end{array}$ derivative, a limit, which, if achieved, would correspond to a stage just below the extreme one, *viz.*, when dry ammonia interacts with sulphur monochloride.

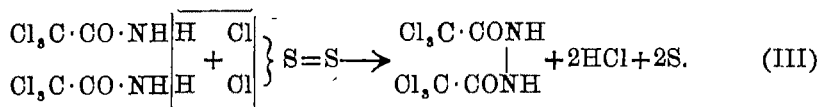
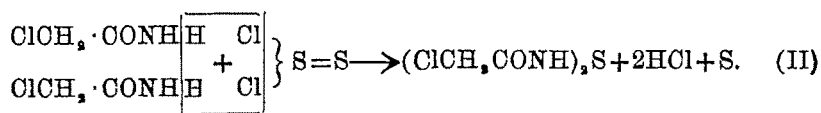
With the above end in view, isobutyramide, valeramide, and capronamide were selected. The reaction with sulphur monochloride in all the three cases followed a very simple course, two molecules of the amide condensing to give a di-amide with profuse evolution of hydrogen chloride and the total elimination of all the sulphur, thus :



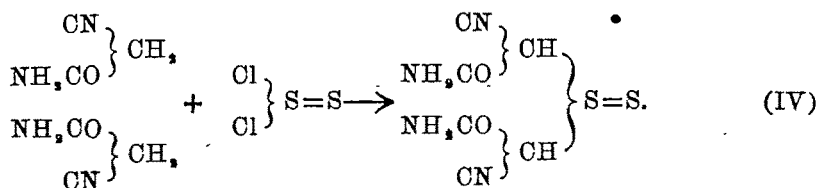
and so on for the others.

These products which showed no trace of sulphur usually had showed higher melting points than the original amides from which they were found to be different by the method of mixed melting points. The molecular weights, too, when determined by the cryoscopic method, gave results in complete accord with those required for the condensed product. Moreover, the di-imido product obtained from capronamide, gave the original amide, on reduction with alcoholic sodium hydrosulphide, thus proving its constitution.

The effect of strengthening the acid group on the reactivity of the amido group, was also studied by selecting monochloracetamide and trichloracetamide as typical examples. Whereas the ammoniacal reactivity of the amido group in acetamide and monochloracetamide was sufficient to give a monosulphide, that in trichloracetamide was reduced to the desired extent and gave the expected di-imido product, thus :

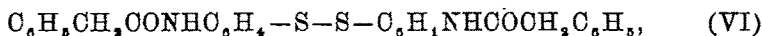
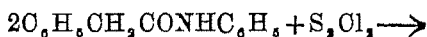
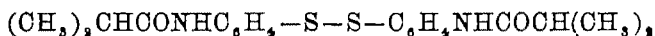
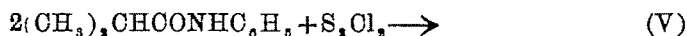


Experiments were also instituted with a view to examine the possibilities of transferring the activity from the amido group in CH_3CONH_2 to the methylene group by substituting one of the hydrogen atoms of the methyl group by acidic groups such as phenyl and cyanogen (*cf.* Naik, T., 1921, 119, 379). The reaction with phenylacetamide was inconclusive, and is being investigated more thoroughly, whilst in the case of cyanacetamide the reactivity was found to be transferred from the amido to the methylene group, thus :

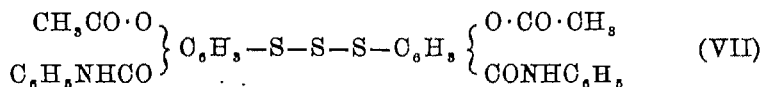
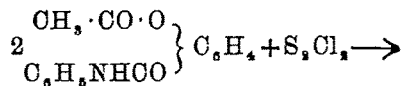


The reaction was very vigorous, as was the case with cyanacetic ester (Naik, T., 1921, 119, 1232).

Further, the reactions of sulphur monochloride with substituted amides such as isobutyranilide, phenylacetanilide, and acetyl salicylanilide were studied. Whereas isobutyranilide and phenylacetanilide gave a disulphide, thus resembling the reaction of salicylamide, (*loc. cit.*) :



acetylsalicylanilide gave a trisulphide, resembling the reactions of acetanilide and benzanilide with sulphur monochloride :



On nitration of the disulphide resulting from (VI), a tetranitroderivative was obtained as before (*loc. cit.*).

EXPERIMENTAL

Symm-dicaproyl hydrazine.

Capronamide (3 grams) and sulphur monochloride (2 grams) were separately dissolved in dry petroleum (25 c.c. for each) and boiled under a reflux condenser. The reaction started with evolution of hydrogen chloride.

After three hours the flask was allowed to cool and a viscous mass deposited at the bottom. The excess of sulphur monochloride was washed away with dry petroleum and the product was kept overnight in vacuum in an alkali desiccator. On being boiled with animal charcoal in benzene and filtered, it deposited from the clear filtrate on cooling, in plates with pearly lustre, and melted on recrystallisation at 111–112°C. The original amide melted at 98°C, while the mixture of the two melted at 95°C. It was easily soluble in benzene, alcohol, acetone and warm water, more difficultly soluble in chloroform, insoluble in petroleum and carbon disulphide.

Molecular Complexity.—A specimen recrystallised from benzene and carefully dried gave the following molecular complexity by the cryoscopic method in this solvent; 0.0102 grams and 0.0152 grams dissolved in 20 c.c. of benzene depressed the freezing point by 0.011°C and 0.019°C, respectively; $M=265, 229$ (average 247). $C_{12}H_{24}O_2N_2$ requires $M=228$. (Found : $N=12.39$. $C_{12}H_{24}O_2N_2$ requires $N=12.28$ per cent.). There was no sulphur in the compound.

Reduction.—5 grams of the above compound were dissolved in 50 c.c. of absolute alcohol and an aqueous solution of sodium hydrosulphide and caustic soda was gradually added (Brand, Ber., 1906, 42, 3464). On cooling a crystalline precipitate was obtained. The crystals were washed free from alkali with hot water and the product on recrystallisation from alcohol melted at 98°C. It was found to be pure capronamide.

Symm-divaleryl hydrazine.

Valeramide (3 grams) and sulphur monochloride (2.5 grams) were separately dissolved in dry petroleum (15 c.c. in each case), mixed and boiled. Hydrogen chloride began to evolve on heating this mixture. The brown viscous

solid deposited on completion of reaction (3 hours), gave shining pearly plates from benzene, as in the case of capronamide, which melted at 123°C . It was soluble in benzene, alcohol, acetone and also in warm water, but insoluble in petroleum and carbon bisulphide.

Molecular Complexity.—0.0194 gram of the substance dissolved in 20 c.c. of benzene depressed the freezing point by 0.025°C ; $M=222$. $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_2$ requires $M=200$. (Found : $\text{N}=14.25$. $\text{C}_{10}\text{H}_{20}\text{O}_2\text{N}_2$ requires $\text{N}=14.00$ per cent.). Sulphur was found to be absent.

Symm-di-isobutyryl hydrazine.

Isobutyramide (3 grams) and sulphur monochloride (3 grams) dissolved in dry petroleum (50 c.c.) were boiled under a reflux condenser. Copious evolution of hydrogen chloride was observed. After treatment of the brown viscous residue in the same way as before, pearly white plates melting at $120\text{--}121^{\circ}\text{C}$ were obtained. The product was found to be easily soluble in benzene, alcohol and acetone, but only slightly soluble in chloroform.

Molecular Complexity.—0.0088 grams of the substance dissolved in 20 c.c. of benzene depressed the freezing point by 0.014°C . $M=180$. $\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$ requires $M=172$. (Found : $\text{N}=16.20$. $\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{N}=16.28$ per cent.). The compound contained no sulphur.

N-sulphidolies-chloracetamide.

A mixture of monochloracetamide (3 grams) and sulphur monochloride (3 grams) in 50 c.c. of dry benzene was boiled till the evolution of hydrogen chloride ceased. A white solid was gradually deposited. The reaction was stopped after 6 hours, the product filtered, washed free from sulphur monochloride and crystallised from hot alcohol, when it was obtained in shining white crystals. It begins to melt at 165°C (decomp.), forming a yellow liquid.

(Found : $N=13.14$; $S=14.5$; $Cl=32.26$. $C_4H_5O_2N_2Cl_2S$ requires $N=12.90$; $S=14.75$ and $Cl=32.72$ per cent.).

Symm-hexachlordiacetyl hydrazine.

Trichloracetamide (6 grams) and sulphur monochloride (2 grams) were boiled in dry benzene (50 c.c.) as in the previous case. A brisk evolution of hydrogen chloride was noted. On cooling a yellowish white mass was deposited which on being freed from the excess of sulphur monochloride and sulphur, was crystallised from benzene and obtained in the form of white needles. On recrystallisation from benzene it melted at $148-149^\circ C$. Trichloracetamide melts at $140^\circ C$.

Molecular Complexity.—0.0423 grams of the substance dissolved in 20 c.c. of benzene depressed the freezing point by $0.035^\circ C$. $M=338$. $C_4H_5O_2N_2Cl_6$ requires $M=323$. (Found : $N=8.80$; $Cl=65.80$. $C_4H_5O_2N_2Cl_6$ requires $N=8.67$ and $Cl=65.94$ per cent.). No sulphur was detected in this compound.

Cyanacetamide-C-disulphide.

Cyanacetamide (3 grams) and sulphur monochloride (3 grams) were boiled in dry benzene (50 c.c.). A brown granular mass was obtained as the evolution of hydrogen chloride proceeded quickly. On completion of the reaction (after 4 hours), the excess of sulphur monochloride was removed by hot benzene. The product was freed from sulphur by being repeatedly boiled under a reflux condenser with carbon disulphide until the melting point became constant. It melts at $103^\circ C$ (decomp.) ; it is insoluble in benzene, petroleum and carbon disulphide, and hydrolyses in alcohol. On standing it undergoes slow decomposition to a dark mass. (Found : $N=24.77$; $S=27.73$. $C_6H_5O_2N_4S_2$ requires $N=24.34$ and $S=27.82$ per cent.).

Symm-di-isobutyryl-diamino-diphenyl disulphide.

Isobutyranilide (3 grams) and sulphur monochloride

(3 grams) were boiled together in dry benzene (50 c.c.) for 12 hours. The resulting pink coloured solution was slowly evaporated in a current of dry hot air, when an indigo coloured mass was obtained. On boiling in benzene with animal charcoal and leaving the solid mass obtained on evaporation of the solvent benzene, in an alkaline desiccator, it was freed from the hydrogen chloride with which it was at first contaminated. The resulting granular mass was redissolved in benzene from which it was deposited in the form of an indigo coloured amorphous granular powder melting at $100-102^{\circ}\text{C}$ (decomp.), very easily soluble in benzene forming a beautiful violet coloured solution and also soluble in alcohol and acetone. (Found : $\text{N}=7.55$; $\text{S}=16.9$. $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{S}_2$ requires $\text{N}=7.22$ and $\text{S}=16.5$ per cent.).

Symm-diphenyl-diacetyl-diamino-diphenyl-disulphide.

Equal quantities (5 grams) of phenylacetanilide and sulphur monochloride were boiled together in dry benzene (50 c.c.) for 15 hours. The excess of sulphur monochloride was then evaporated in a draught of dry air, the viscous solid residue redissolved in benzene and precipitated by petroleum. It melted at 162 to 163°C . (Found : $\text{N}=5.68$, $\text{S}=12.98$. $\text{C}_{28}\text{H}_{24}\text{O}_2\text{N}_2\text{S}_2$ requires $\text{N}=5.79$ and $\text{S}=13.22$ per cent.).

Symm-tetranitro-diphenyl-diacetyl-diamino-diphenyl-disulphide.

Two grams of the above substance were gradually treated with 10 c.c. fuming nitric acid (S. G. 1.5), keeping the temperature low. At first a sudden evolution of the oxides of nitrogen took place, the disulphide going into solution at the same time. The liquid was slightly concentrated, allowed to cool and filtered, when on slight dilution with water, a very pure yellowish mass was

obtained, which melted at 148—150°C (decomp.). (Found : $N=12.76$; $S=9.23$. $C_{28}H_{20}O_{10}N_6S_2$ requires $N=12.65$ and $S=9.64$ per cent.).

Symm-diacetoxy-dianilino-diformyl-diphenyl-trisulphide.

Acetylsalicylanilide (4 grams) were boiled in dry benzene (100 c.c.) with sulphur monochloride (3 grams) for eighteen hours. After the evaporation of the solution in a current of dry air, the dirty white viscous mass obtained was redissolved in benzene and boiled with animal charcoal. The clear filtrate was allowed to drop into a large quantity of petroleum ether, when a partly granular and partly viscous mass was obtained. This was left in an alkaline desiccator overnight, dissolved in benzene and precipitated by petroleum in the form of a light yellow powder which melted at 78°C (decomp.). (Found : $S=15.62$. $C_{30}H_{24}O_6N_2S_3$ requires $S=15.89$ per cent.).

THE CHEMICAL LABORATORIES,

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[Received May 31, 24]

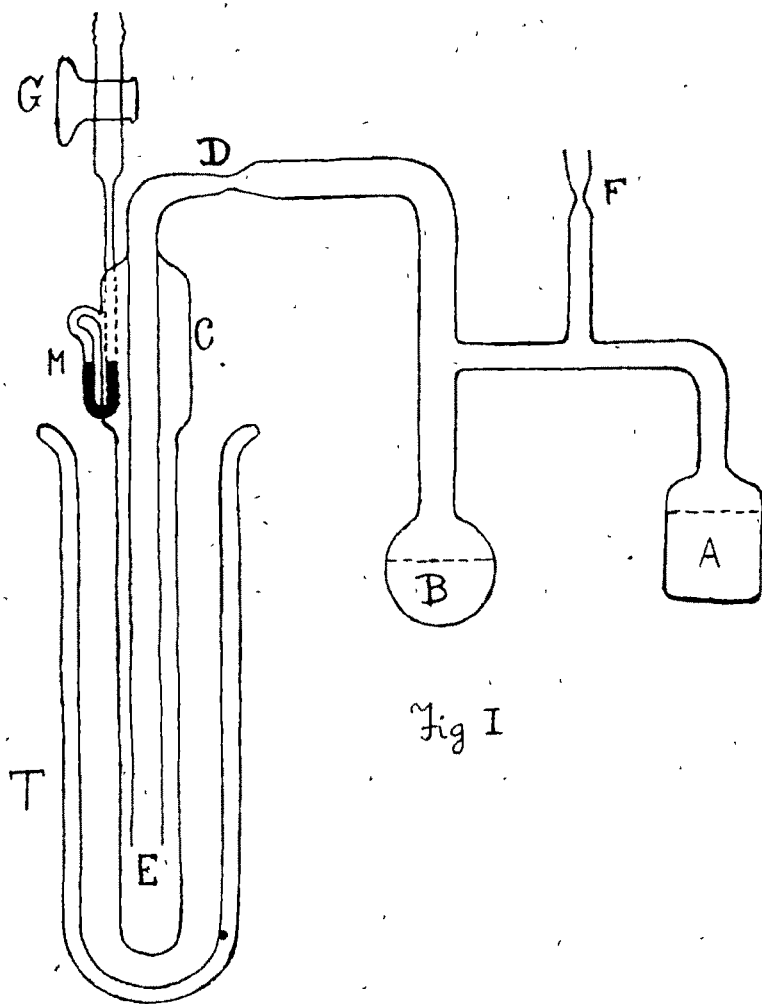


Fig I

On the Vapour Pressure and Chemical Constant of Formaldehyde.

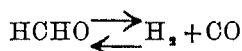
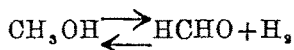
BY

SASIBHUSHAN MALI

AND

JNANENDRACHANDRA GHOSH.

In course of investigations now in progress on the study of the reactions



it was found necessary to investigate the physical properties of pure formaldehyde in order that the conditions of equilibrium governing the above reactions might be theoretically ascertained. The Nernst Heat theorem could be applied to the above reactions, if the Chemical Constant of pure formaldehyde and its latent heat of vaporisation at various temperatures could be found out,—the corresponding data for the other molecular species taking part in the reactions being already known.

Preparation of Pure Liquid Formaldehyde.

Gaseous formaldehyde is an extremely fugitive substance; it becomes very easily transformed into solid paraform and various other solid polymerisation products. Kekule¹ succeeded in obtaining liquid formaldehyde by heating dry paraform and condensing the gas produced.

¹ Ber. 1892, 25, 2435.

Various methods were tried for preparing pure formaldehyde vapour—the one recommended by Sachs¹ which consisted in heating oxymethyl-phthalimide appeared promising. But it was ultimately found that consistent data on the physical properties of formaldehyde could only be had when formaldehyde was obtained from paraform which had been thoroughly dried by anhydrous phosphorous pentoxide. Even then it was found that if the temperature of liquid formaldehyde were raised above -30°C , transformation into solid polymerisation products became very rapid, and the results became untrustworthy; below -30°C however, the liquid keeps unchanged indefinitely.

Fig. 1 gives the experimental arrangement for collecting pure liquid formaldehyde in the experimental tube.

A—Phosphorous pentoxide tube plugged with glass wool.

B—Paraform (Kahlbaum's purest) tube protected by an asbestos mantle.

C—Experimental tube dipped in liquid air contained in a Dewar flask.

M—Manometer U tube, the bent portion of which is filled with mercury.

E—The point where formaldehyde condensed.

F and G—for connection to vacuum pump.

The whole apparatus was evacuated, stopcock G closed and F sealed, and paraform was allowed to dry in vacuum for a fortnight. Paraform in B was then heated and dry formaldehyde was condensed at E by means of liquid air. Care should be taken that the end of the delivery tube at E does not get choked with solid formaldehyde. After sufficient formaldehyde had collected, the experimental tube was sealed off at D.

¹ Ber. 1899, 31, 1231.

*Measurement of Vapour Pressure of Liquid
Formaldehyde.*

As has been observed before, formaldehyde vapour begins to condense as a solid whose vapour pressure is almost zero at temperatures above -30°C . This unique behaviour makes it necessary to have a pressure-recording device which could be maintained at temperatures below -30°C . Otherwise a part of the vapour will condense as solid in the measuring instrument, where the pressure will necessarily fall, and a gradient of pressure will thus be established from the surface of the liquid to the point where the pressure is being recorded. To obviate this difficulty, a thin glass tube M was attached to the experimental tube C, and was bent close to its sides in the form of U. The mercury column at M remained dipped in the liquid of thermostat where the temperature did not exceed -30°C , but was not below about -35°C , and hence during the measurement of pressure no solid paraform could condense on the surface of the mercury in M. The experimental arrangements are given in Fig. 2.

T is a wide Dewar flask about four-fifths filled with liquid air. T' is another unsilvered Dewar flask dipped in T with a side tube at the top, which by means of a Vollmer pump, creates a vacuum variable at will, in the annular space. For very low temperatures, a good vacuum is essential. It contained pure acetone up to the top in which dipped the experimental tube containing liquid formaldehyde.

Stirrer.—The stirrer consisted of a thick tube of copper attached to the end of two stout iron wires. At the bottom of the tube were attached several fine copper filaments at right angles, to help agitation. It was moved up and down about 10 cms. from the bottom by means of an eccentric pulley run by a hot air motor.

Heating Coil.—Round the copper tube of the stirrer, as near to the bottom as possible, was wound a heating coil of silk-covered constantan wire insulated by means of thin mica. The leads passed up along the stout iron wires of the stirrer and ended in the terminals of a storage battery. Current from the battery was regulated by a rheostat, and thus the thermostat liquid could be heated up to any desired temperature.

Temperature Gradient in the Thermostat Liquid.

The temperature is lowest at the bottom, and is highest at the top, due to contact with air of the room. Due to the movement of the copper cylinder stirrer, the temperature within about 8 cms. from the bottom remains constant. Beyond that, the temperature gradually rises, and this rise becomes very rapid as the level of liquid air in the outer flask T is passed. In the region of M, the temperature could, with a certain amount of manipulation be maintained constant at about -30°C .

Thermocouple.—A copper constantan couple was used, the electromotive force being given by the Nernst formula

$$E = 31.32T \log\left(1 + \frac{T}{90}\right) + 1 \times 10^{-7}T^4$$

$$\text{or } E - E_1 = 31.32T \log\left(1 + \frac{T}{90}\right) + 1 \times 10^{-7}T^4 - 31.32T_1 \log\left(1 + \frac{T_1}{90}\right) + 1 \times 10^{-7}T_1^4$$

where if T is the absolute temperature of the hot junction (that of ice-bath), the cold junction being at *absolute zero*, E is the E. M. F. in microvolts; T_1 the temperature of liquid air thermostat and the difference $E - E_1$ is the E. M. F. actually observed between the thermostat temperature and the ice-bath outside. The cold junction was near at the bottom of the thermostat close to the side of the experimental tube where a few cc. of liquid formaldehyde was present. The couple had been previously

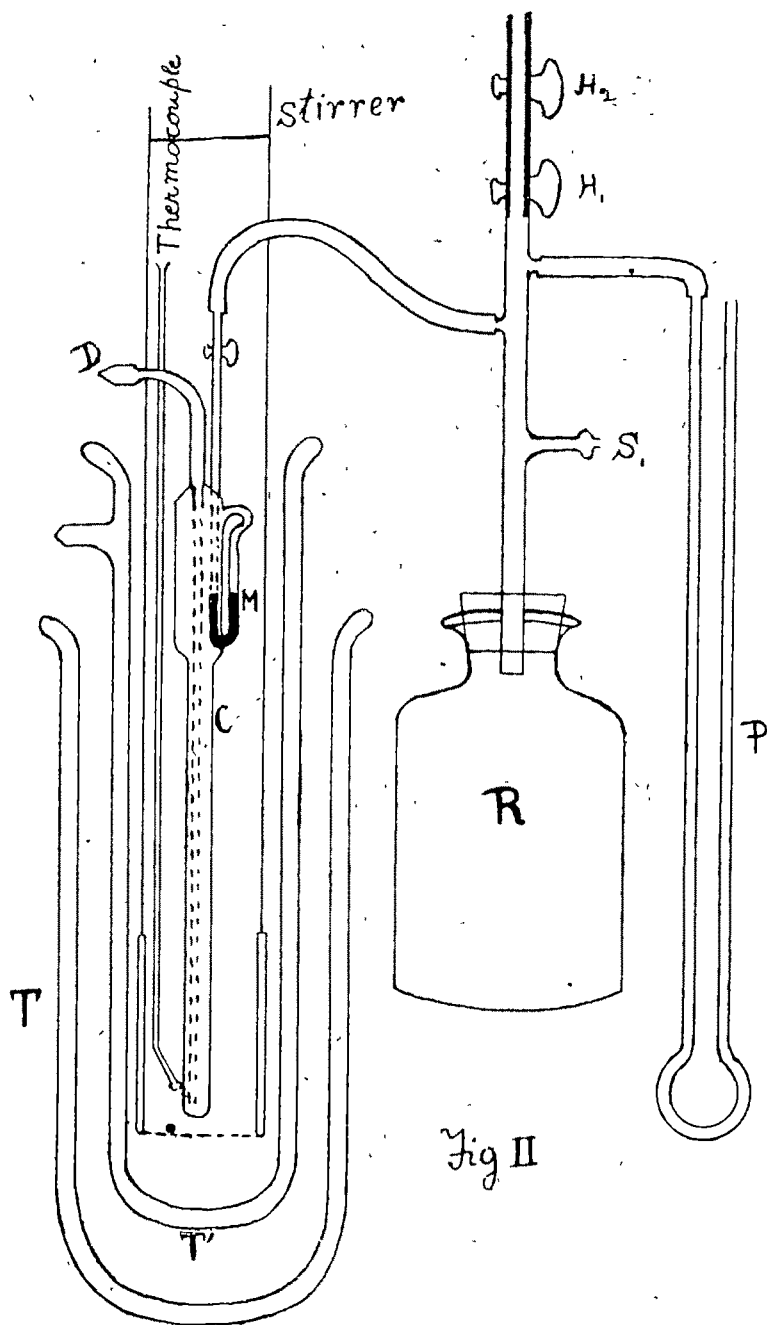


Fig II

used to measure the temperature of melting mercury and the temperature was found to be -38.6°C .

D—The experimental tube C after immersion in the thermostat which had already attained constant temperature, was broken open at D and connected to a high vacuum pump which chased away the last trace of air, and then closed. To prevent the displacement of the mercury column during the evacuation the manometer M was connected to a pump and evacuated simultaneously.

Reservoir.—R. Pressure of air in this reservoir was rendered equal to that of liquid formaldehyde—the equality being indicated by the mercury column in M. This was done by decreasing the pressure in the reservoir by evacuation through the side tube S_1 and then increasing by carefully opening and closing stopcocks H_1 and H_2 joined together by a capillary tubing.

P—Manometer connected to air reservoir; the difference in the levels of the mercury columns was measured by means of a kathetometer.

Experimental Results and Discussion.

The vapour pressure of formaldehyde at various temperatures are given below

-91°C	1.00 cm.
$-55^{\circ}.5\text{C}$	14.25 cms.
$-46^{\circ}.8\text{C}$	23.7 cms.
$-41^{\circ}.8\text{C}$	30.45 cms.
$-34^{\circ}.5\text{C}$	41.4 cms.

According to Nernsts' simplified equation, the vapour pressure of a liquid can be expressed by an equation of the type

$$\ln p = -\frac{\lambda_0}{RT} + \frac{3.5}{R} \ln T - \frac{c}{R} T + (i + \ln R)$$

or
$$\log p = -\frac{\lambda_0}{2 \cdot 3RT} + \frac{3 \cdot 5}{R} \log T - \frac{\epsilon T}{2 \cdot 3R} + C$$

where C is the Chemical Constant of the liquid. The experimental data recorded above agree with the equation

$$\log p = -\frac{6500}{4 \cdot 6T} + 1 \cdot 75 \log T - \frac{0 \cdot 035 T}{4 \cdot 6} + 3 \cdot 3$$

where P is expressed in atmospheres and the heat energy in calories. The latent heat of evaporation at absolute zero is 6500 and the chemical constant = 3.3. It is obvious that an equation containing three unknown constants λ_0 , ϵ and C can undergo a good deal of relative variation in the values of these constants without greatly affecting the values of P, and hence their values fixed as above cannot be very accurate. If, however, ϵ is determined independently from measurements of specific heat, the equation would only contain two unknown variables λ_0 and C and their values could be fixed from measurements of P without much uncertainty. Measurement of specific heat of formaldehyde is in progress and the value of C given above is only tentative. It is to be noted that the Chemical Constant of formaldehyde (3.3) is identical with that of ether, and slightly less than that of acetone (3.7), but very much less than that of ethyl alcohol 4.1.

Troutons' Law.—The boiling point of formaldehyde was approximately -21°C . From the Nernst formula (Wärmesatz, p. 125)

$$\lambda = (\lambda_0 + 3 \cdot 5T - \epsilon T^2) \left(1 - \frac{p}{\pi_0} \right)$$

where p is the pressure at the temperature at which λ is to be calculated and π_0 the critical pressure,

Neglecting $\frac{p}{\pi_0}$ compared to unity, we obtain

$$\lambda = 6500 + 3.5 \times 252 - 0.035 \times (252)^2 \\ = 5160 \text{ calories.}$$

Applying Troutons' Rule, we have $\frac{\lambda}{T} = \frac{5160}{252} = 20.5$ units of entropy.

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Studies on Phototropism in Solution.

Part II.

The Optical Activity as an Aid in the Study of Phototropy.

BY

BAWA KARTAR SINGH.

In Part I of this series of investigations (J. Amer. Chem. Soc., 1921, 43, 333), the author described some new cases of phototropism which exhibit the phenomenon in solution only. These were α -naphthylaminocamphor, *m*-phenylenebisaminocamphor and *ar*-tetrahydro- α -naphthylaminocamphor when dissolved in chloroform. With one possible exception, namely, di-9-hydroxy-phenyl-anthryl-10-amine (Foresti, *Atti R. accad. Lincei*, 1914, (V), 23, 270) phototropy had not previously been observed except in the case of solids.

The object of the present paper is to describe some experiments which have been carried out with one of these optically active phototropic substances, namely, α -naphthyl-aminocamphor, in which the phototropic change has been followed by means of a polarimeter.

The term phototropism was originally applied to reversible isomeric changes in solid substances produced by light and accompanied by change of colour. Since the above discovery by the author (*loc. cit.*), no such limitation with regard to the state of aggregation of the substance is recognised, and the term is equally applied to include all isomeric changes in substances in solution induced by light and accompanied by change of colour.

Phototropism in the Solid State.

The phenomenon was originally noticed by Marckwald (Zeitsch. Physikal. Chem., 1899, 30, 140) in the case of

the yellow hydrochloride of quinoquinoline which changes to green in light, and reverts to the original colour in the dark and in that of β -tetrachloro- α -ketonaphthalene, which is colourless in the dark, and reddish violet in the light. Senier and Shepherd (T., 1909, 95, 441, 1943), found in salicylidene *m*-toluidine, a remarkable photo-reactive substance. It is pale yellow in colour. On exposure to sunlight, it changes to deep orange, and reverts to its original colour when placed in the dark. The change brought about by light is much faster than the reverse change. The spectroscopic evidence shows that the change from the pale-coloured to the dark-coloured modification is due to the activity of the light rays of high refrangibility. The change does not take place in solution, in which case only the pale-coloured modification appears to exist. The phenomenon exhibited by salicylidene *m*-toluidine thus opened a new and interesting field of research, and Senier and Shepherd (*loc. cit.*), examined a number of Schiff's bases, out of which only a few turned out to be phototropic, though most of them were thermotropic. Those which exhibit phototropy are derived from salicylaldehyde, in which the substituents are in the ortho position. The substitution of hydroxyl by methoxyl destroys the phototropic effect entirely.

The differences in colour produced by light in phototropic substances undoubtedly depend on some kind of isomeric change. The molecules of solids are far more complex than those of liquids and gases, and in fact their molecular magnitude is practically unknown. They may be regarded as aggregates of ordinary gaseous molecules. Consequently Senier and Shepherd (*loc. cit.*) suggest that the phototropic behaviour of solids is not due to intramolecular change, but to extramolecular rearrangement of simple molecules into molecular aggregates.

Phototropism in Solution.

The optically active substances which exhibit remarkable phototropic reactions in solution are very suitable for studying the course of the change, which can be conveniently followed by means of rotatory power determination. The yellow sodium light is unsuitable as it cannot pass through the green solution obtained after exposure to sunlight. The mercury green light ($\lambda=5461$) is easily transmitted through the solution for a considerable depth of colour, and is therefore employed in following the change. In this paper, a preliminary account of some experiments carried out with α -naphthylaminocamphor is given. A more detailed study of the phenomenon with this and other compounds is reserved for a future communication.

The following polarimetric experiment made with a chloroform solution of α -naphthylaminocamphor shows that the intensity of the colour and the rotatory power of the solution increase with the time of exposure to direct sunlight, and that the reverse change in the dark takes place much more slowly.

0.726 gram of the substance made up to 100 ccs. gave the following values for rotatory power at 30° :—

Time of exposure to—

(a) light (minutes)				[α]5461
0	126.0
1	137.0
2	149.0
3	160.3
4	168.5
5	178.0
6	186.6
7	too dark to read.
(b) dark (hours)				
23	168.0

A second polarimetric experiment illustrates the

influence of sodium ethoxide on the phototropic change. The addition of a drop of an alcoholic solution of sodium ethoxide to a chloroform solution of α -naphthylaminocamphor entirely inhibits the phototropic change. The solution to which no sodium ethoxide is added, undergoes the usual photo-reaction.

0.73 gram made up to 100c.cs. gave the following results :—

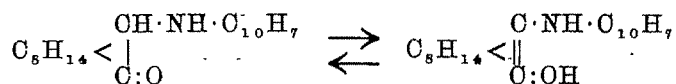
	[α]5461 With sodium ethoxide	[α]5461 Without sodium ethoxide
(a) before exposure	110°	137°
(b) 2 days in dark followed by 5 minutes' exposure to sunlight...	113	170

The photo-reaction of α -naphthylaminocamphor in chloroform solution is dependent on the nature of the light employed. Under the influence of light waves of high refrangibility (blue rays), the colourless chloroform solution changes to green, and when removed from that influence it returns to its original colour. The orange or red light is practically without any effect.

The phototropic change of α -naphthylaminocamphor also depends on the nature of the solvent, in which it is dissolved. The effect is only noticed in chloroform, in which it dissolves as a colourless solution, and it remains so if it is kept in the dark, but on exposure to sunlight the colour becomes deep bottle green within a minute. In the dark the green colour vanishes completely in about 24 hours. In other solvents, namely, acetone, methyl alcohol, ethyl alcohol, ether, petroleum ether, and ethyl acetate, the colour changes which take place on exposure to sunlight, are comparatively very slow and are irreversible. The colour developed in these cases varies from light yellow to deep yellow and the time required for the colour to appear varies from half-an-hour to five hours. It therefore seems that chloroform is the

only solvent in which the reversible photo-reaction can be observed.

These results run parallel with the colour reactions which α -naphthylaminocamphor dissolved in the same solvents gives with ferric chloride. With the chloroform solution of the substance, ferric chloride gives a port wine colour before exposure to light and reddish brown colour after exposure; it thus indicates the presence of enol modification in it. Solutions in ethyl alcohol and ethyl acetate (in which the reversible photo-reaction is not observed) do not produce any colour, characteristic of hydroxy compounds, with ferric chloride both before and after exposure to light. This shows that in these solvents, the substance exists in the keto form only. It therefore, follows that only the chloroform solution of the substance is an equilibrium mixture of the keto-enol modifications of the following type:—



The addition of sodium ethoxide to the chloroform solution shifts the above equilibrium so that it contains the enol modification only. In this case also the solution does not undergo the phototropic change. It would therefore, appear that for the occurrence of the phototropic change both the keto and enol modifications should be present together in solution.

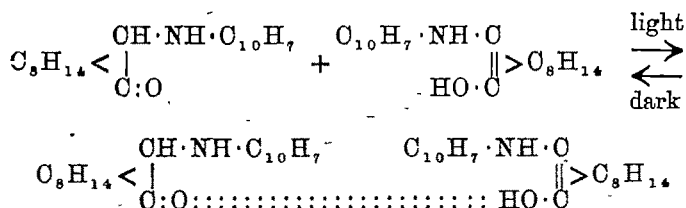
The keto modification $\text{C}_8\text{H}_{14} < \begin{array}{c} \text{OH} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7 \\ | \\ \text{C}:\text{O} \end{array}$ represents the substance as a mono-aryl derivative of aminocamphor. It ought, therefore, to be colourless.

The enol modification $\text{C}_8\text{H}_{14} < \begin{array}{c} \text{C} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7 \\ || \\ \text{O}:\text{OH} \end{array}$ should also be colourless, as the chloroform solution of the substance in the presence of sodium ethoxide is colourless.

In the former paper (*loc. cit.*) the author had suggested that the green colour of the solution may be due to the enol modification. This view seems to be now disproved by the foregoing arguments.

The phototropic change of α -naphthylaminocamphor in chloroform is due, therefore, not to the change of the keto to the enol form. It occurs only when both the modifications are present together in solution and is accompanied by the formation of a green substance, and by a marked increase in the rotatory power of the solution.

It may be tentatively suggested that the phototropic change is due to the mutual interaction of keto and enol modifications of the substance with the production of a compound of the "quinhydrone" type:—



The colour of such a compound could be explained in the same way by which Willstätter (Ber., 1908, 41, 1458, 3245) explained the colour of quinhydrones.

The non-occurrence of the phototropic change in solvents in which no enolisation takes place, as well as the similar influence of sodium ethoxide in which case only the enol modification exists, can both be explained on this hypothesis. The above explanation of the phototropic change is only provisional, and is to be tested by further experiments.

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Thiodiazines.

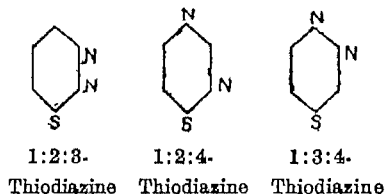
Part I.

Condensation of Thiosemicarbazide with ω -Bromacetophenone.

BY

PRAFULLA KUMAR BOSE.

Thiodiazole derivatives have been studied by numerous investigators chiefly by Max Busch and his collaborators, but there is lack of information regarding the chemistry of thiodiazines. An examination of the literature showed that of the six possible classes of thiodiazines, a few representatives of the following three types only are known, namely,

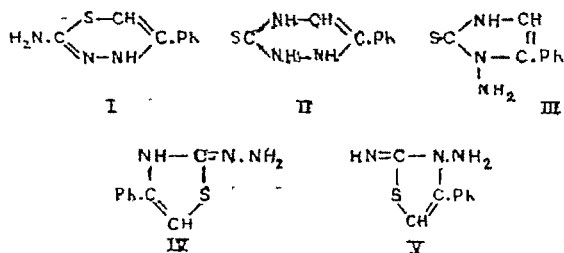


Schrader (J. pr. Chem., 1917, [2], 96, 180) obtained a derivative of 1:2:3-thiodiazine by condensing *o*-cyano-benzenesulphonyl chloride with hydrazine. Again a derivative of 1:2:4-thiodiazine has been obtained by the oxidation of 2-phenylimino-3-phenyl-tetrahydrothiazole, (Kucera, Monats., 1914, 35, 137; compare also Schrader, J. pr. Chem., 1916, [2], 95, 392); while the only derivative of 1:3:4-thiodiazine is that obtained by Frerichs and Förster (Annalen, 1910, 371, 236, 255). It might be mentioned here that the so-called 1:3:4-thiodiazines obtained by the condensation of potassium aryl-sulphocarbazonates with ethylene dibromide (Busch, Ber., 1894, 27, 2509, 2516; Busch and Lingenbrink, J. pr. Chem., 1899, [2], 60,

219, 225) have afterwards been proved to be arylhydrazones of cyclic dithiocarbonic ester (Busch and Lingenbrink, J. pr. Chem., 1902, [2], 65, 473). Another so-called thiodiazine derivative, 2-amino-4-phenyl-5-keto-dihydro-1 : 3 : 4-thiodiazine obtained by condensing phenylhydrazine with sulphocyanacetic acid (Harries and Klamt, Ber., 1900, 33, 1154) has been shown by Frerichs and Förster (*loc. cit.*) to be a thiohydantoin derivative. Evidently, excepting the very few derivatives of the thiodiazines referred to above, no other representatives of this class of compounds are known. An investigation has therefore been taken up with a view to obtain further knowledge on the subject. In the present communication, which is of a preliminary character, the condensation of thiosemicarbazide with ω -bromacetophenone has been described and the constitutions of the reaction products determined.

On boiling an alcoholic solution of the reactants in molecular proportion, the hydrobromide of a base of the empirical composition, $C_9H_9N_3S$ (m. p. 125°) separates in brownish-yellow needles melting at 196° , while the mother liquor on being treated with acetone in the cold gave a crystalline hydrobromide (m. p. $225-26^\circ$ not sharp,) of another compound of the empirical formula $C_{11}H_{13}N_3S$ which melted at 123° .

The condensation of ω -bromacetophenone with thiosemicarbazide might lead to the formation of the following possible isomeric compounds.



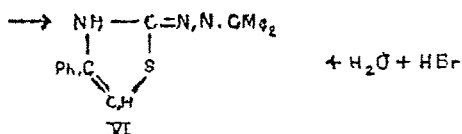
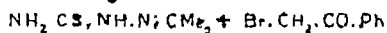
The absence of acid character of the substance, (m. p. 125°), coupled with its inability to lose sulphur when boiled with alkaline lead solution or freshly precipitated yellow mercuric oxide, precludes the possibility of its possessing a $-\text{NH-CS-NH}$ or $-\text{NH-CS-N=}$ residue in the molecule as represented in formulæ (II) and (III) (compare Guha, J. Am. Chem. Soc., 1922, 44, 1511). Moreover, it is well-known that a halogenated ketone acts on thiocarbamides forming compounds containing sulphur atom in the ring (compare Walther and Roch, J. pr. Chem., 1913, [2], 87, 27). Again the compound under discussion has been found lacking in the capacity to condense with acetone or anisaldehyde, which should not be the case, had it possessed any free hydrazino group as formulated in (IV) and (V). On the other hand, the chemical evidence based on its actions towards phenylthiocarbimide, carbon disulphide and benzene sulphonyl chloride points definitely to the presence of a free amino group in the molecule. All these facts are best interpreted by the formula (I), which has consequently been assigned to the compound.

2-Amino-5-phenyl-1:3:4-thiodiazine (I) is a strong monoacid base and forms well-defined salts with acids. It gave a picrate and an aurichloride. The acetyl and benzoyl derivatives are soluble in alkali.

Attempt was made to prepare the isomeric acetyl compound, 2-amino-5-phenyl-3-acetyl-1:3:4-thiodiazine, by the action of ω -bromacetophenone upon 1-acetylthiosemicarbazide. The reaction took place readily in alcoholic solution producing the hydrobromide of an acetyl compound which is soluble in alkali. The alkaline solution, however, unlike that of its isomer, develops a beautiful greenish-blue colour on exposure to air, which turns pink on being acidified. On boiling with an excess of dilute hydrochloric acid, the acetyl compound

suffered a smooth hydrolysis yielding a crystalline base (m. p. 167-68°) isomeric with 2-amino-5-phenyl-1:3:4-thiodiazine (I). On further examination it was found to behave like substituted hydrazine since it readily condensed with acetone and anisaldehyde. The acetone condensation product appeared to be identical with the base, $C_{12}H_{13}N_3S$ (m. p. 123°) obtained by adding acetone to the condensation product of thiosemicarbazide and ω -bromacetophenone (*vide supra*). It might, therefore, be reasonably assumed that the reactions in both the cases have proceeded in such a way that the hydrazino residue of the thiosemicarbazide has been left unattacked. Consequently the constitution of the base, m. p. 167-68°, might be represented by (IV) or (V).

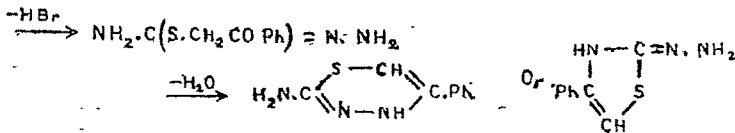
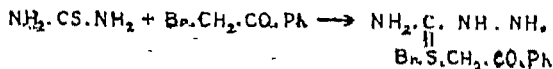
In order to obtain clear evidence in support of one or other of these two formulæ, acetone-thiosemicarbazone was condensed with ω -bromacetophenone. The resulting hydrobromide, as also the base proved to be identical with the acetone condensation products mentioned before. Now acetone-thiosemicarbazone has been shown to react with alkyl halides producing compounds of the type $NH_2 \cdot C(SAlk):N:N:OMe_2$ (Wilson and Burns, T., 1922, 121, 870). In other words, the hydrogen atom attached to the nitrogen atom in position 2, is responsible for the tautomeric thiol-form. From the close analogy therefore, one might expect that the condensation of ω -bromacetophenone and acetone-thiosemicarbazone proceeds thus:



The base, $C_{12}H_{13}N_3S$, m. p. 123° is thus proved to be 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole-isopropylene

hydrazone (VI), and the base, $C_8H_8N_3S$, m. p. $167-68^\circ$, to be 2-keto-4-phenyl 2:3-dihydro-1:3-thiazole hydrazone (IV). The condensation of thiosemicarbazide with ω -bromacetophenone becomes therefore interesting in as much as it leads to the simultaneous formation of a five-membered as well as a six-membered heterocyclic ring.

With respect to the mechanism of condensation, the author suggests that the first stage consists in the addition of the bromoketone to the sulphur atom of the thiosemicarbazide with the formation of an intermediate sulphonium derivative. (Compare, Dixon and Taylor, T., 1912, 101, 2502; Walther and Roch, J. pr. Chem., 1913, [2], 87, 27). This is followed by the elimination of hydrobromic acid forming S-phenacylthiosemicarbazide, which in the final stage loses a molecule of water resulting in ring closure, which might occur in two ways, thus:



The proportion of the thiodiazine and the thiazole derivatives, the author is inclined to think, will depend on the relative basic character of the two amino groups present in the thiosemicarbazide molecule. Since the basic character of the 1-amino group is much more enhanced than that of the 4-amino group, the main product of reaction is the thiodiazine, the quantities of the thiodiazine and the thiazole derivatives being actually in the ratio, 5 : 1. It follows from what has been assumed that the condensation of thiosemicarbazide derivatives in which the basic character of the 1-amino group has been suppressed will result in the formation of a thiazole

derivative. The production of the acetyl derivative of 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole hydrazone from 1-acetyl-thiosemicarbazide and ω -bromacetophenone confirms this deduction.

EXPERIMENTAL.

Thiosemicarbazide and ω -Bromacetophenone: Formation of 2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole-isopropylene hydrazone (VI) and 2-Amino-5-phenyl-1:3:4-thiodiazine (I).—4.5 grams (1 mol.) of thiosemicarbazide and 10 grams (1 mol.) of ω -bromacetophenone were heated under reflux with 50 c. c. of dry ethyl alcohol for 15-20 minutes. The dark reddish-brown solution was then concentrated to nearly one-third its volume and cooled, when clusters of brownish yellow needles of the hydrobromide of (I) began to appear. These were freed from the mother liquor, washed with dry ethyl alcohol and finally with acetone. The yield of the crude hydrobromide, m. p. 192-95°, was about 8.6 grams or about 64% of the theoretical. The mother liquor was diluted with its own volume of dry acetone and the colorless plates (m. p. 225-26°) of the hydrobromide of (VI) which immediately began to appear, were collected after an hour. The yield was about 2.1 grams or about 14% of the theoretical. The latter hydrobromide was dissolved in hot water containing a few drops of methyl alcohol, filtered and the solution made alkaline with sodium carbonate. The crystalline precipitate of 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole-isopropylene hydrazone (VI) was crystallised from dilute methyl alcohol in colorless hexagonal plates melting at 123°, which turned reddish brown on exposure to light for some time. (Found: C=62.20; H=5.85. $C_{12}H_{13}N_3S$ requires C=62.35; H=5.63 per cent.).

The former hydrobromide (m. p. 192-95°) separates from a 95% alcoholic solution by the addition of ether, in snow-white needles melting at 197°, after the usual treatment with animal charcoal. (Found: N=15.27; Br=29.86; S=11.34. $C_9H_{10}N_3SBr$ requires N=15.54; Br=29.41; S=11.77 per cent.). To obtain the free thiodiazine the crude hydrobromide (8.6 grams) was dissolved in about 150 c.c. of warm water and allowed to stand for an hour. The solution was then filtered to remove a small amount of a brownish yellow impurity and made alkaline with a solution of sodium carbonate. The solution at once turned milky and within a few minutes gave a mass of colorless needles of *2-amino-5-phenyl-1:3:4-thiodiazine* (I). These were filtered after half an hour, washed with cold water and dried on a porous plate. The compound was purified by repeatedly dissolving in cold dilute hydrochloric acid filtering off any insoluble matter and precipitating with dilute sodium carbonate solution. It melted at 125-26°. (Found: C=56.80; H=4.69; N=22.05; S=17.07. $C_9H_9N_3S$ requires C=56.55; H=4.71; N=21.99; S=16.76 per cent.). The base is very soluble in most organic media from which it is difficult to obtain it in the crystalline form on dilution with suitable solvents. On exposure to air, (especially when moist) or in solution, it gradually turns brown owing to oxidation.

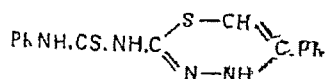
The *hydrochloride* of the base separates from a mixture of alcohol and ether in colorless rectangular plates melting at 205° decomp. (Found: Cl=15.44; S=14.18. $C_9H_{10}N_3SCl$ requires Cl=15.60; S=14.07 per cent.). The *picrate* was obtained in the form of golden yellow plates melting at 213° decomp., on mixing the components in alcoholic or acetone solution. The *aurichloride* was obtained by treating a hydrochloric acid solution of the base with a dilute aqueous solution of auric

chloride. It crystallised from hot water in golden yellow needles melting at $166-67^{\circ}$ decomp. (Found : $\text{Au}=37.19$; $\text{Cl}=26.30$. $\text{C}_9\text{H}_{10}\text{N}_3\text{SO}_4\text{Au}$ requires $\text{Au}=36.98$; $\text{Cl}=26.79$ per cent.).

The *acetyl* derivative was obtained by treating the base with acetyl chloride in pyridine solution in the cold. From glacial acetic acid it separates in colorless needles melting at $172-73^{\circ}$. (Found : $\text{N}=18.07$. $\text{C}_{11}\text{H}_{11}\text{ON}_3\text{S}$ requires $\text{N}=18.03$ per cent.). The *benzoyl* derivative, obtained in a similar manner, crystallises from dilute pyridine in colorless needles melting at 170° . (Found : $\text{N}=14.7$; $\text{C}_{16}\text{H}_{18}\text{ON}_3\text{S}$ requires $\text{N}=14.24$ per cent.). The acetyl and benzoyl compounds are soluble in aqueous alkali; acids precipitate them from solution in white amorphous mass.

2-Amino-5-phenyl-1:3:4-thiodiazine and Methyl Iodide.—A methyl alcoholic solution of the base was heated with an excess of methyl iodide under reflux for 5-6 hours on the water bath when the hydroiodide of 2-methylamino-5-phenyl-1:3:4-thiodiazine (?) separates in colorless needles. It was recrystallised from 95% alcohol and ether in colorless prismatic needles melting at 223° decomp. (Found : $\text{N}=13.09$; $\text{I}=39.11$. $\text{C}_{10}\text{H}_{12}\text{N}_3\text{SI}$ requires $\text{N}=12.62$; $\text{I}=38.14$ per cent.). The hydroiodide of the ethylation product, which crystallises in colorless rectangular plates and melts at 234° decomp., could be similarly obtained. These hydroiodides are soluble in hot water. On treating the aqueous solution with alkali or sodium carbonate colorless oils were obtained which failed to crystallise.

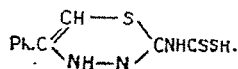
2-Amino-5-phenyl-1:3:4-thiodiazine and Phenylthiocarbimide : Formation of



The reactants were heated in alcoholic solution in molecular proportion for a few minutes, when yellow crystals of the above thiocarbamide separated out. From pyridine it was obtained in bright yellow plates melting at 179-80°. (Found: N=16.65. $C_{16}H_{14}N_4S_2$ requires N=17.18 per cent.).

2-Phenylsulphonylamino-5-phenyl-1:3:4-thiodiazine.—To one molecule of the above base were added two molecules of alcoholic caustic potash and then with constant shaking an alcoholic solution of one molecule benzene sulphonyl chloride. The reaction was completed by heating on the water bath for a few minutes. On cooling colorless needles were obtained. These were recrystallised from alcohol, the first fraction being rejected. The product which appeared to be the potassium salt of the complex sulphonamide was however not very pure. (Found: S=9.82. $C_{15}H_{13}O_2N_3SK$ requires S=8.68 per cent.). It was very soluble in water. The free sulphonamide could not be obtained pure owing to its hygroscopic nature and extreme solubility in water and other organic media.

2-Amino-5-phenyl-1:3:4-thiodiazine and Carbon Disulphide: Formation of



A mixture of the base (1 mol.), alcoholic caustic potash (1 mol.) and carbon disulphide in excess was heated on the water bath under reflux for 8-10 hours. The excess of carbon disulphide was distilled off, the liquid separated from a small amount of an oily residue and the free dithiocarbamic acid precipitated by acidifying with dilute hydrochloric acid. The yellow product was dissolved in aqueous alkali, treated with animal charcoal and reprecipitated by hydrochloric acid. From absolute

alcohol it separates in yellow needles melting at 181-82° decomp. (Found : N=15·97 ; S=35·30. $C_{10}H_9N_3S_3$ requires N=15·73 ; S=35·96 per cent.).

The *monomethyl* derivative was obtained by dissolving the dithiocarbamic acid in the calculated amount of methyl alcoholic potash and heating under reflux for half an hour with an excess of methyl iodide. The reaction mixture on being concentrated by evaporation deposited the methyl ether in bright yellow hexagonal plates, which melted at 159°, after crystallisation from dilute pyridine. (Found : C=46·76 ; H=4·09. $C_{11}H_{11}N_3S_3$ requires C=46·98 ; H=3·92 per cent.)

1-Acetylthiosemicarbazide and ω -Bromacetophenone : Formation of 2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole-acetylhydrazone.—Equimolecular quantities of the components were heated in *dry* alcoholic solution for a few minutes. On cooling the *hydrobromide* of 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole-acetyl hydrazone was deposited in colorless needles melting at 234-35° decomp. The hydrobromide was dissolved in 80 per cent. alcohol and treated with an excess of aqueous ammonia when the free acetyl compound was obtained. It separated from hot alcohol, after treatment with animal charcoal, in pinkish needles melting at 196-97° decomp. (Found : C=56·08 ; H=5·16. $C_{11}H_{11}ON_3S$ requires C=56·65 ; H=4·72 per cent.). The acetyl compound is soluble in alkali. The alkaline solution develops a beautiful greenish blue colour in presence of air, which turns pink when acidified. The colour totally vanishes after a few hours.

Hydrolysis of 2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole-acetylhydrazone.—The acetyl compound was heated with a large excess of dilute hydrochloric acid (2N approx.) for about an hour until a test portion on being made alkaline with caustic soda and shaken with air did not turn blue. The whole solution was then made alkaline

with caustic soda when *2-keto-4-phenyl-2:3-dihydro-1:3-thiazole hydrazone* (IV) was precipitated in dirty white needles. This was rapidly filtered at the pump, redissolved in dilute hydrochloric acid, filtered from a small amount of brown oxidation product and precipitated with sodium carbonate solution. It was finally crystallised from alcohol in long colorless needles melting at 167-68°. (Found: C = 56.00; H = 4.24. $C_9H_9N_3S$ requires C = 56.55; H = 4.71 per cent.). It possesses strong basic properties and forms well-defined salts with acids. The moist base on exposure to air turns brown owing to oxidation.

2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole hydrazone and Acetone: Formation of (VI).—The reactants were boiled together for a few minutes and the solution evaporated to dryness. The brown residue was taken up with methyl alcohol, decolorised with animal charcoal, and precipitated by cautious addition of water in hexagonal plates melting at 123°. The substance turns brown on exposure to light. (Found: N = 17.87. $C_{13}H_{13}N_3S$ requires N = 18.18 per cent.).

2-Keto-4-phenyl-dihydro-1:3-thiazole-anisal hydrazone.—This was obtained by the condensation of *2-keto-4-phenyl-2:3-dihydro-1:3-thiazole hydrazone* and anisaldehyde as a beautiful yellow compound when a dilute hydrochloric acid solution of the hydrazone was shaken with anisaldehyde. From alcohol it separates in pinkish white needles melting at 225° decomp. (Found: N = 13.35. $C_{17}H_{15}N_3S$ requires N = 13.59 per cent.).

Condensation of Acetonethiosemicarbazone and ω -Bromacetophenone: Formation of (VI).—1.3 grams of the former and 2 grams of the latter were boiled under reflux with 30 c.c. of dry alcohol for about 15 minutes. The condensation product separated from the boiling mixture in colorless plates melting at 235° decomp., and appeared to be identical with the hydrobromide (m. p. 225-26° not

sharp) obtained by the addition of acetone to the mother liquor of the condensation product of thiosemicarbazide and ω -bromacetophenone. The hydrobromide was dissolved in very dilute (10%) methyl alcohol and poured into a dilute solution of sodium carbonate. The crystalline precipitate was thoroughly washed with water and finally crystallised from dilute methyl alcohol in hexagonal plates melting at 123° . (Found: C=62.80; H=5.86. $C_{12}H_{13}N_3S$ requires C=62.35; H=5.63 per cent.).

Hydrolysis of 2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole-isopropylene hydrazone: Formation of (IV).—The hydrazone was boiled for a few minutes with concentrated hydrochloric acid and the solution was evaporated to dryness on the water bath. The residue was taken up with cold water, filtered and made alkaline with sodium carbonate. The resulting base was several times recrystallised from alcohol until the melting point reached 168° . (Found: N=22.03. $C_9H_9N_3S$ requires N=21.99 per cent.). This compound was found to be identical with the product of hydrolysis of 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole-acetyl hydrazone (*vide supra*).

The work is being continued with substituted thiosemicarbazides and monochloracetone, monochloracetal and esters of α -halogenated acids

In conclusion, I take this opportunity of expressing my sincere thanks to Sir P. C. Rây for his keen interest throughout this investigation.

COLLEGE OF SCIENCE,

UNIVERSITY OF CALCUTTA.

[Received May 29, 24].

Varying Valency of Gold with respect to Mercaptanic Radicles.

Part I.

BY

SIR PRAFULLA CHANDRA RÂY.

In continuation of the study on the varying valency of platinum (Rây, T., 1923, 123, 133) that of gold has recently been undertaken. In the present communication have been described some bi-, ter-, quadri-, and quinque-valent gold compounds, showing thereby that the valency of gold like that of platinum is variable with respect to mercaptanic radicles.

Bi-, Ter-, and Quadri-valent Gold.

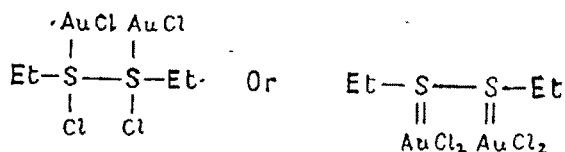
The starting mercaptanic derivative in this case also was diethyldisulphide, which on treatment with gold chloride (chlorauric acid), yielded a crystalline compound having the empirical formula EtS.AuCl_2 , to which may at first sight be assigned the graphic formula,

$\text{EtS.Au} \begin{smallmatrix} \text{Cl} \\ < \\ \text{Cl} \end{smallmatrix}$ the gold behaving as tervalent. This

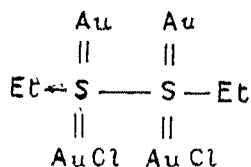
formula seemed to be unlikely as it would imply that during the reaction, the disulphide had undergone scission, thus: $\text{EtS} \begin{smallmatrix} \vdots \\ | \\ \vdots \end{smallmatrix} \text{SEt}$. Moreover, the product of

the corresponding reaction with platinic chloride had the formula $\text{Et}_2\text{S}_2\text{PtCl}$, which has been shown to be a derivative of quinquevalent platinum and a sulphonium compound as well (*loc. cit.*). It was natural to suppose that the simple formula of the gold compound should be doubled, that is, it should be $\text{Et}_2\text{S}_2.2\text{AuCl}_2$.

Determination of the molecular weight by the freezing point method has justified this conclusion. The compound can thus be represented as

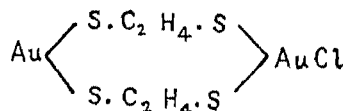


according as the gold is taken to function as bi- or quadri-valent. This constitutional formula of the chloromercaptide brings it into intimate relationship with the numerous sulphonium iodomercaptide derivatives, which the author has been studying during the last ten years (T., 1916, 109, 131, 603; 1917, 111, 101, etc.), where it is shown that the so-called "molecular compounds" of the type $\text{R}_2\text{S}_2 \cdot \text{HgI}_2 \cdot \text{R'I}$ are in reality "atomic compounds" of the sulphonium type. Diethyldisulphide also furnishes another compound with gold chloride having the empirical formula $\text{Et}_2\text{S}_2 \cdot \text{Au}_4\text{Cl}_2$. Its constitution may be represented as



where sulphur is sexavalent and gold alternately bi- and ter-valent. Instances of chain compounds of sexavalent sulphur have already been given (Ray, T., 1919, 115, 548).

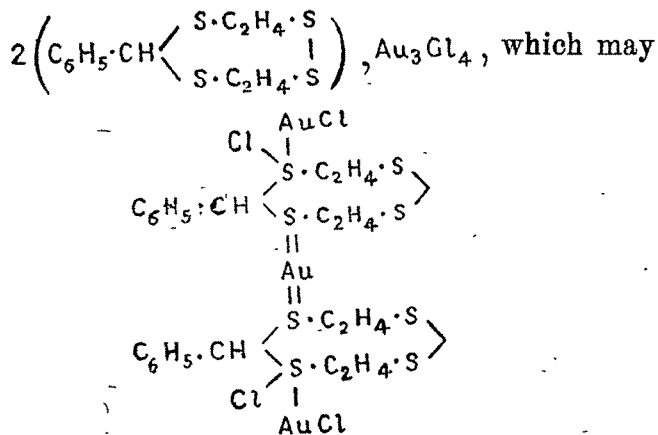
Bivalent gold evidently occurs in the compound $\text{Au}_2\text{Cl}(\text{C}_2\text{H}_4\text{S})_2$ —the product of the interaction of the monopotassium mercaptide (Ray, T., 1923, 123, 133) and gold chloride. It may be graphically represented as



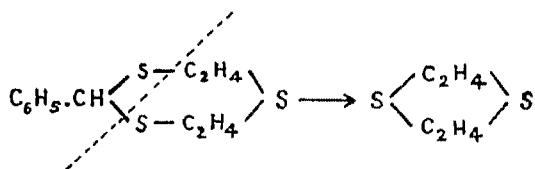
one atom of gold behaving as bi- and the other as ter-valent.

Benzaldiene tetrasulphide (Ray, T., 1924, 125, 1141) on treatment with gold chloride yielded the compound, conforming to the formula

be represented as



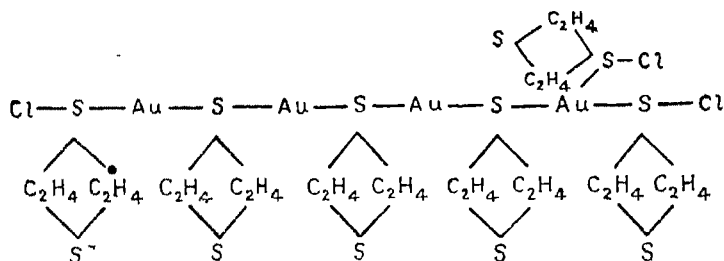
the gold functioning alternately as bi- and quadri-valent. When, however, benzaldiene trisulphide is similarly treated it has the structure broken up according to the scheme :



diethylene disulphide (1:4-dithian) being the degradation product. Evidently this scission takes place on account of the molecule being loaded with the heavy radicles of gold chloride. It has been shown in the previous communication (*loc. cit.*) that mercuric chloride and even a light radicle like methyl iodide brings about similar rupture. Representing the dithian molecule by A, the following compounds have been obtained : (a) 6A, Au₄Cl₃ ;

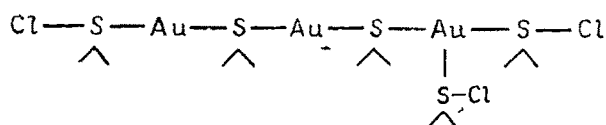
(b) $5\text{A}, \text{Au}_3\text{Cl}_5$; (c) $4\text{A}, \text{Au}_3\text{Cl}_4$; (d) $4\text{A}, \text{Au}_3\text{Cl}_2$; (e) $3\text{A}, \text{Au}_3\text{Cl}_2$ and (f) $3\text{A}, \text{Au}_3\text{Cl}_2$. In all these cases the temperature of the reaction varied as a rule from 28° to 55° . In one special case both the component solutions were heated to 78° and the resulting compound had the formula $3(\text{C}_2\text{H}_4\text{S}_2)\text{Au}_3\text{Cl}_2$ (g), the 1:4-dithian molecule yielding a still simpler degradation product, namely, ethylene disulphide. It might be urged that there is the possibility of some of these compounds being contaminated with traces of reduced gold or of being mixtures. An alcoholic solution of gold chloride has, no doubt, been sometimes found to turn slightly turbid in course of a quarter of an hour or so, but the reactions involved were finished in less than a couple of minutes; moreover, within wide limits of temperature and concentration of the reacting components as also in both alcoholic and ethereal solutions the identical compound, *e.g.*, compound (a) has often been obtained. Hence the chances of their being mixtures are precluded.

The anomalous nature of these chlorides can be easily explained if the atoms of gold be taken as bi- and ter-valent respectively as in the instances cited above. Thus $6\text{A}, \text{Au}_4\text{Cl}_3$ may be represented as



in which only one atom of sulphur of each of the dithian molecules becomes quadrivalent, the sulphur atoms at the extreme ends of the chain taking up the chlorine atoms, thus converting it into a sulphonium compound.

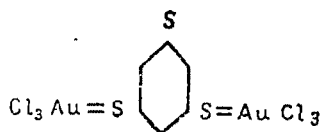
5A, Au_3Cl_5 may from this point of view be looked upon as



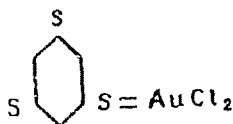
The other complex chlorides may similarly be graphically represented. It will thus be seen that the determining factor in the formation of these chlorides is the greater affinity of sulphur atoms for those of gold—the latter preferring to enter into combination with it and liberating chlorine (compare, Rây, T., 1923, 123, 134).

Quinquevalent Gold.

Triethylene trisulphide (Rây, T., 1920, 117, 1090) by interaction with gold chloride has yielded two compounds, namely, $(\text{C}_2\text{H}_4\text{S})_3 \cdot 2\text{AuCl}_3$ and $(\text{C}_2\text{H}_4\text{S})_3 \cdot \text{AuCl}_2$. The former may be represented as

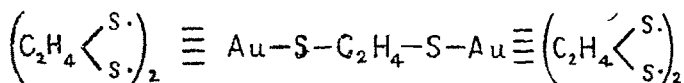


in which the gold functions as quinquevalent; similarly the second compound may be represented as

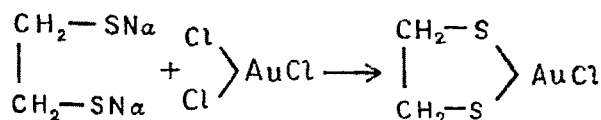


in which the gold functions as quadrivalent.

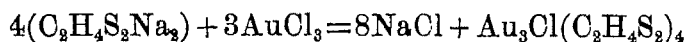
Direct proof of the quinquevalency of gold has also been obtained by the formation of the compound



by the interaction of sodium dithioethylene glycol and gold chloride in acetone solution. The corresponding platinum compound has also been isolated. The disodium mercaptide was also treated with an ethereal solution of gold chloride. It was anticipated that the reaction would proceed as follows



but the compound actually obtained had the formula $(\text{C}_2\text{H}_4\text{S}_2)_4\text{Au}_3\text{Cl}$. The reaction no doubt takes place according to the equation :



EXPERIMENTAL.

Bi-, Ter-, and Quadri-valent Gold.

Action of Gold Chloride on Diethyl Disulphide.—The disulphide was treated with an excess of an aqueous solution of gold chloride and continuously stirred. At first a pasty deep yellow mass was obtained, which on 'teasing' with a rod solidified into a crystalline product. It was further purified by recrystallisation from boiling toluene. (Found: Au=59·90; Cl=21·39; S=10·25. $\text{C}_4\text{H}_{10}\text{S}_2\text{Au}_2\text{Cl}_4$ requires Au=59·90; Cl=21·58; S=9·73 per cent.). The determination of the molecular weight by the freezing point method (in naphthalene) gave the result as 655, 666·8 and 670·3 respectively, the calculated molecular weight being 658. The compound when dissolved in naphthalene slowly deposits particles of gold; care should therefore be taken to finish the operation within half an hour. The determination of the molecular weight by the ebullioscopic method (in toluene) gave unsatisfactory

results for similar reasons. In fact, the separation of gold in this case is much more rapid. The compound slowly darkens on exposure to light due to separation of fine particles of gold. If, however, the above reaction be not allowed to go beyond the pasty stage and the mass extracted with ether, a portion goes into solution and the ethereal extract on spontaneous evaporation deposits a white amorphous powder, which conforms to the formula $\text{Et}_2\text{S}_2, \text{Au}_4\text{Cl}_2$ (Found: $\text{Au}=79.36$; $\text{Cl}=7.45$; $\text{S}=7.76$. Theory requires $\text{Au}=80.33$; $\text{Cl}=7.24$; $\text{S}=6.53$ per cent.). The crystalline insoluble residue was found to be identical with the previous compound.

Action of Gold Chloride on Disodium Dithio-ethylene Glycol.—To the dimercaptide suspended in ether was added an ethereal solution of gold chloride. Reaction at once commenced and the mixture was heated under reflux for 3-4 hours. A light brown precipitate put in an appearance. It was filtered and washed with water several times and dried in a vacuum over sulphuric acid. (Found: $\text{Au}=59.90$; $\text{S}=25.55$; $\text{Cl}=3.75$. $\text{C}_8\text{H}_{16}\text{S}_2\text{Au}_3\text{Cl}$ requires $\text{Au}=59.42$; $\text{S}=25.74$ and $\text{Cl}=3.57$ per cent.).

Action of Gold Chloride on Monopotassium Dithioethylene Glycol.—In the case of platinum it has already been found that the particular valency which the metal might take up depends upon the concentration as also the temperature of the participants (Ray, T., 1923, 123, 133). Similar *modus operandi* was adopted in this case. 12 c.c. of gold chlorine solution (1 c.c. = 0.0260 gm. Au) were added to 0.5500 gm. of the potassium salt of dithioethylene glycol dissolved in 15 c.c. of water at 5° , 28° , 65° and 80° in different preparations. A brown precipitate was formed in each case. It was washed with water, alcohol and ether and dried in a vacuum. All the preparations were found to be identical in composition. (Found: $\text{Au}=62.23$;

Cl=4.65; S=21.18. $C_4H_8S_4Au_2Cl$ requires Au=62.39; Cl=5.62 and S=20.27 per cent.).

Action of Gold Chloride on Benzaldiethylene Tetrasulphide.—An alcoholic solution of gold chloride was added in a thin stream under vigorous agitation to an ethereal solution of the sulphide. A flocculent reddish precipitate was formed. It was washed with ether and dried in a vacuum. It had the formula $2[C_6H_5CHS_4(C_2H_4)_2], Au_3Cl_4, (C_2H_5)_2O$.^{*} (Found: Au=42.40; Cl=10.53; S=19.70. $C_{28}H_{38}OS_8Au_3Cl_4$ requires Au=43.62; Cl=10.48; S=18.89 per cent.). The same compound was also obtained when both the components were mixed in ethereal solution. From the filtrate of the latter again a further quantity of a precipitate with identical composition was obtained.

Action of Gold Chloride on Benzaldiethylene Trisulphide.—(a) *Expt. 1.*—0.1940 gm. of the sulphide was dissolved in 5 c.c. of alcohol. To it was added 2 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0510 gm. Au). The reaction was carried out at 55°. *Expt. 2.*—The same quantity of the sulphide was dissolved in 10 c.c. of alcohol and to it was added 3 c.c. of gold chloride of the same strength as above. The temperature of the reaction was 40°. *Expt. 3.*—The same quantity of the trisulphide was this time dissolved in 15 c.c. of alcohol and to it was added 3 c.c. of gold chloride. The temperature of the reaction was 30°. *Expt. 4.*—0.1730 gm. of the sulphide was dissolved in 4 c.c. of alcohol and to it was added 8 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0155 gm.

* In these and the compounds of gold and platinum to be subsequently described a molecule or more of ether or alcohol of combination, as the case may be, often occurs. (Compare Rây, T, 1924, 125, 1143) The filtrate from the product of reaction of benzaldiethylene trisulphide and platinum chloride (*loc. cit.*) in alcohol deposited a compound of the formula $C_{11}H_{14}S_3 \cdot PtCl_2 \cdot 3EtOH$. (Found. Pt=30.45; Cl=9.85; C=31.26; H=4.73. Theory requires Pt=30.40; Cl=10.96; C=31.48; H=4.93 per cent.)

Au) at 28°. *Expt. 5.*—0.2160 gm. of the sulphide was dissolved in 5 c.c. of alcohol and to it was added 10 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0155 gm. Au). The temperature of the reaction was 50°. In each of these cases the compounds obtained had identical composition. The formation of one and the same compound within wide limits of temperature and concentration also precludes the possibility of their being any mixtures. It conformed to the formula $6[(C_2H_4)_2S_2], Au_4Cl_3$. (Found: Au=49.06; Cl=6.78; S=23.52. $C_{24}H_{48}S_{12}, Au_4Cl_3$ requires Au=48.79; Cl=6.79; S=23.77 per cent.).

(b) 0.2474 gm. of the trisulphide was dissolved in 5 c.c. of ether and cooled with ice-water. To it was added an excess of gold chloride in ether (1 c.c.=0.0273 gm. Au) under vigorous agitation. The brown precipitate was washed with ether and dried in a vacuum. It conformed to the formula $5[(C_2H_4)_2S_2], Au_3Cl_3, 1\frac{1}{2}(C_2H_5)_2O$. (Found: Au=42.00; Cl=12.18. Theory requires Au=42.03; Cl=12.62 per cent.).

(c) In this experiment the components were dissolved in ethereal solution and were mixed in indefinite proportions. The compound had the formula $4[(C_2H_4)_2S_2], Au_3Cl_4, \frac{1}{2}(C_2H_5)_2O$. (Found: Au=47.61; Cl=11.42. Theory requires Au=47.38; Cl=11.36 per cent.).

(d) 0.1300 gm. of the sulphide was dissolved in 3 c.c. of alcohol and heated to about 72°. To it was added 10 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0155 gm. Au). The compound obtained had the formula $4[(C_2H_4)_2S_2], Au_3Cl_2$. (Found: Au=52.17; Cl=6.35; S=22.43. Theory requires Au=51.75; Cl=6.22 and S=22.41 per cent.).

(e) 0.4991 gm. of the sulphide was dissolved in alcohol. To it was added drop by drop under constant agitation 1 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0623 gm. Au). A purple precipitate was obtained. It

was washed first with benzene and then with alcohol and dried in a vacuum. Under the microscope it revealed a brown, spongy texture but no gold particles. It conformed to the formula $3[(C_2H_4)_2S_2], Au_3Cl_2, C_2H_5OH$. (Found: Au=55.76; Cl=6.98. Theory requires Au=55.34; Cl=6.65 per cent.).

(f) (*Expt. 1*).—0.3582 gm. of the sulphide was dissolved in 25 c.c. of alcohol and heated on the waterbath to 60°. To it was added an excess of an alcoholic solution of gold chloride (1 c.c.=0.1066 gm Au) all at once and agitated on the waterbath between 60-70°. (*Expt. 2*).—0.2750 gm. of the sulphide was dissolved in 10 c.c. of alcohol and heated to 40-50°. To it was added 6.5 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0425 gm. Au) all at once and vigorously agitated. In both these preparations the compounds had identical composition and conformed to the formula $3[(C_2H_4)_2S_2], Au_3Cl_2, C_2H_5OH$. (Found: Au=45.61, 45.64; Cl=8.43, 8.74; S=23.22, 23.80. Theory requires Au=45.24; Cl=8.15; S=22.04 per cent.).

(g) 0.4110 gm. of the sulphide was dissolved in 30 c.c. of alcohol and heated on the waterbath and to it was added 6.5 c.c. of gold chloride in alcohol (1 c.c.=0.0425 gm. Au) and again heated on the waterbath for a few minutes more. The product agreed with the formula $3[(C_2H_4)_2S_2], Au_3Cl_2, C_2H_5OH$. (Found: Au=60.34; Cl=7.27; S=19.08. Theory requires Au=60.06; Cl=7.22; and S=19.51 per cent.).

Quinquevalent Gold.

Disodium Dithioethylene Glycol.—To an ethereal solution of dithioethylene glycol, very finely divided metallic sodium was added, care being taken to exclude moisture. Slow evolution of hydrogen took place and a fine

crystalline powder of the dimercaptide was formed. (Found: $\text{Na} = 32.71$. $\text{C}_2\text{H}_4\text{S}_2\text{Na}_2$ requires $\text{Na} = 33.84$ per cent.).

Action of Gold Chloride on Disodium Dithioethylene glycol.—The dimercaptide was suspended in acetone and an acetone solution of gold chloride was added. The mixture was digested on the water bath for about an hour. The product had the formula $\text{C}_{10}\text{H}_{20}\text{S}_{10}\text{Au}_2$. (Found: $\text{Au} = 47.38$, $\text{S} = 36.19$,* $\text{C} = 14.05$. Theory requires $\text{Au} = 46.13$, $\text{S} = 37.50$, $\text{C} = 14.00$ per cent.).

Action of Gold Chloride on Triethylene Trisulphide.—Alcoholic solutions of the components were mixed together. An orange-colored precipitate was immediately formed. It conformed to the formula $(\text{C}_2\text{H}_4\text{S})_3.2\text{AuCl}_3$. (Found: $\text{Au} = 50.90$; $\text{Cl} = 26.39$; $\text{S} = 11.03$. $\text{C}_6\text{H}_{12}\text{S}_3\text{Au}_2\text{Cl}_6$ requires $\text{Au} = 50.06$; $\text{Cl} = 27.06$; $\text{S} = 12.20$ per cent.). The alcoholic filtrate containing an excess of gold chloride deposited on spontaneous evaporation, a crop of white crystals of the formula $(\text{C}_2\text{H}_4\text{S})_3. \text{AuCl}_2$. (Found: $\text{Au} = 44.00$; $\text{Cl} = 15.27$; $\text{S} = 20.73$. $\text{C}_6\text{H}_{12}\text{S}_3\text{AuCl}_2$ requires $\text{Au} = 43.97$; $\text{Cl} = 15.87$; $\text{S} = 21.43$ per cent.).

In conclusion, I avail myself of this opportunity to express my cordial thanks to Messrs. Indu Bhusan Sen Gupta and Khitish Chandra Ray for the patience and skill with which they conducted the experimental part of this investigation.

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[Received May 29, 24]

* The estimation was effected by fusion with Na_2CO_3 and KNO_3 . Traces of sulphur are converted into sulphonic acids owing to the presence of the radioc C_2H_4 and hence the percentage of sulphur comes out slightly low. (Compare Ray, T., 1920, 117, 1091)

Absorption of the Halogens by Mercurous Salts.

Part I.

Formation and Properties of some Complex Compounds of Mercury.

BY

KUVERJI GOSAI NAIK

AND

MAHADEO DATTATRAYA AVASARE.

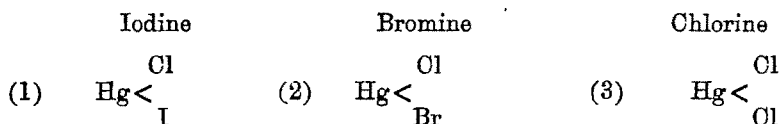
The work undertaken (a preliminary note on which appeared in J. Amer. C. S., Vol. 45 (notes), pp. 2769-70) originated during the course of a mercurial preparation involving the use of calomel for outside application in which it was thought advisable to use iodine, as it was expected that (1) calomel would combine with iodine to form a compound with increased mercurial activity and (2) the iodine being a germicide would contribute favourably to the germicidal properties of the preparation.

The toxicity of mercuric salts is directly related to the ionising capacity of the salts, whilst mercurous salts like calomel, which are insoluble, cannot be absorbed to the necessary extent, and so their use as germicides is limited. It appeared, therefore, that if some way could be found to slightly increase the solubility of these compounds, without very much increasing their degree of dissociation, their usefulness would be greatly enhanced.

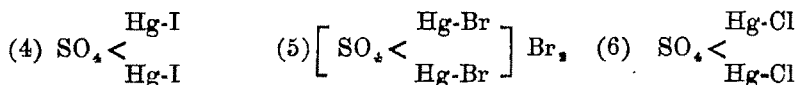
In the work described here the mercurous salts, chloride, sulphate and nitrate were shaken with alcoholic solutions of bromine and iodine. The latter were rapidly

absorbed and gave beautiful crystalline compounds from which attempts were made to produce the corresponding chloro-derivatives by passing dry chlorine gas over them. During the course of this work the following compounds were obtained:—

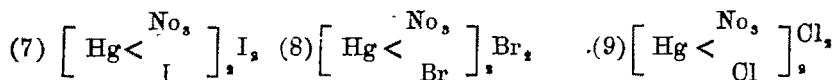
From mercurous chloride—



From mercurous sulphate—



From mercurous nitrate—



Compound (1) has been prepared by Kohler (B. 12, 1187) and by others but in small yield, whilst the method described here is extremely simple and gives quantitative yields of the pure product.

The fact that compound (5) was soluble in boiling water and it was found possible to estimate its bromine quantitatively in the ordinary way as silver bromide from its aqueous solution, as well as the fact that (6), which is derived from (5) by passing chlorine gas over it, is also soluble in water and in which chlorine could be estimated in the usual way, excludes the possibility of such compounds being molecular compounds or double salts having the formulæ $\text{HgSO}_4 \cdot \text{Hg Br}_2$, Br_2 and $\text{HgSO}_4 \cdot \text{HgCl}_2$. For it is well known that under such circumstances mercuric sulphate (and mercuric nitrate as well) would hydrolyse to a basic mercuric salt which will precipitate as a yellow substance. Hence the

mercury atom in such compounds can be suggested to form a part of the molecular complex, which would perhaps render such a preparation therapeutically useful.

The interaction of mercurous nitrate with the halogens gave tetrahalogen derivatives (7), (8) and (9). The bromo- and the chloro- derivatives (8) and (9), like (5), were soluble in a large quantity of boiling water without any hydrolysis and it was from the water solutions that the halogens were estimated in the usual way, confirming the view that all these compounds are not double salts but complex compounds.

EXPERIMENTAL

(1) *Mercurio Ohloriodide*

Two grams of powdered calomel were shaken with an alcoholic solution of iodine in a stoppered bottle at room temperature. The iodine began to be rapidly absorbed. After the absorption of the iodine ceased, the solution was kept for some days and a beautiful red crystalline compound was obtained. It was re-crystallised from alcohol. It changed from red to yellow at 125° and melted to a yellow liquid at 153° . Yield three grams.

(Found : Cl = 9.58; I = 35.22. HgClI requires Cl = 9.79; I = 35.03 per cent.)

The compound, though insoluble in water, dissolved readily in alcohol.

(2) *Mercuricchlorbromide*

Four grams of finely powdered calomel were shaken with an alcoholic solution of bromine as before, when the bromine was found to be rapidly absorbed with rise of temperature. The reaction mixture was consequently kept at room temperature by slightly cooling it under the tap. When bromine ceased to be absorbed, the

solution was allowed to evaporate to remove the excess of bromine, when a syrupy liquid was obtained which yielded a white crystalline mass on standing over sulphuric acid in a desiccator. It slowly sublimes without melting, when heated in a melting point tube. (Found: Cl = 11.23 ; Br = 24.98. HgClBr requires Cl = 11.26 ; Br = 25.36 per cent.)

The compound was freely soluble in alcohol, sparingly soluble in cold water, and easily soluble in boiling water.

When its solution in water is treated with silver nitrate, silver bromide is quantitatively precipitated.

On passing dry chlorine over mercuric chloriodide (1), at room temperature in a tube open at both ends, and driving away the excess chlorine by means of dry carbon dioxide, a white mass was obtained which when crystallised from alcohol was found to be identical with mercuric chloride (HgCl_2).

(4) *Di-iodo-dimercuric sulphate*

This compound was obtained as a red crystalline mass by shaking mercurous sulphate with an alcoholic solution of iodine under the conditions stated above. When crystallised from alcohol it turned yellow at 143° and melted at 248° . Yield quantitative.

(Found: I = 33.87. $\text{Hg}_2\text{SO}_4\text{I}_2$ requires I = 33.86 per cent.)

The compound though insoluble in water was soluble in alcohol.

(5) *Tetrabromodimercuric sulphate*

On treating mercurous sulphate with an alcoholic solution of bromine, under the conditions already described, a syrupy liquid was obtained, which deposited a white crystalline mass when left to crystallise in a desiccator over sulphuric acid. On recrystallisation from

alcohol, it was found to decompose at 125° and melt with decomposition at 235° .

(Found: $\text{Br}=39.17$; $\text{Hg}=49.10$; $\text{SO}_4=11.78$. $\text{Hg}_2\text{SO}_4\text{Br}_4$ requires $\text{Br}=39.21$; $\text{Hg}=49.03$; $\text{SO}_4=11.77$ per cent.)

The compound was found to be sparingly soluble in cold water, more in boiling water. It dissolved freely in alcohol. When allowed to stand in air it slowly emitted vapours of bromine. Silver bromide was quantitatively precipitated from its solution in water by the addition of silver nitrate.

(6) *Di-chlorodimercuric sulphate*

When dry chlorine gas was passed over (5) tetrabromodimercuric sulphate, a white amorphous mass was obtained which when crystallised from alcohol began to darken at 175° and melted at 270° .

(Found: $\text{Cl}=12.50$. $\text{Hg}_2\text{SO}_4\text{Cl}_2$ requires $\text{Cl}=12.52$ per cent.)

It is sparingly soluble in cold water, more in hot water and freely soluble in alcohol. Its halogen was estimated in the usual way from its water solution.

(7) *Tetraiododimercuric nitrate*

Mercurous nitrate was shaken with an alcoholic solution of iodine, as before. The resulting red compound was crystallised from alcohol, when it changed to yellow at $145\text{--}146^{\circ}$ and melted at 250° . Yield quantitative.

(Found: $\text{I}=49.22$. $\text{Hg}_2(\text{NO}_3)_2\text{I}_4$ requires $\text{I}=49.23$ per cent.)

(8) *Tetrabromodimercuric nitrate*

This compound was prepared in the same way, as its corresponding iodo derivative, using an alcoholic solution of bromine in place of iodine. The resulting liquid, after the excess of bromine was allowed to go away, gave on

standing over sulphuric acid in a desiccator, a white crystalline substance, which on subsequent re-crystallisation from alcohol, yielded a compound which decomposed on heating.

(Found: Br=38.02. $\text{Hg}_2(\text{NO}_3)_2\text{Br}_4$ requires Br=37.91 per cent.)

The compound was very soluble in alcohol, appreciably soluble in cold water and more in hot water without decomposition. The halogen was estimated in the usual way from its water solution.

(9) *Tetrachlorodimercuricnitrate*

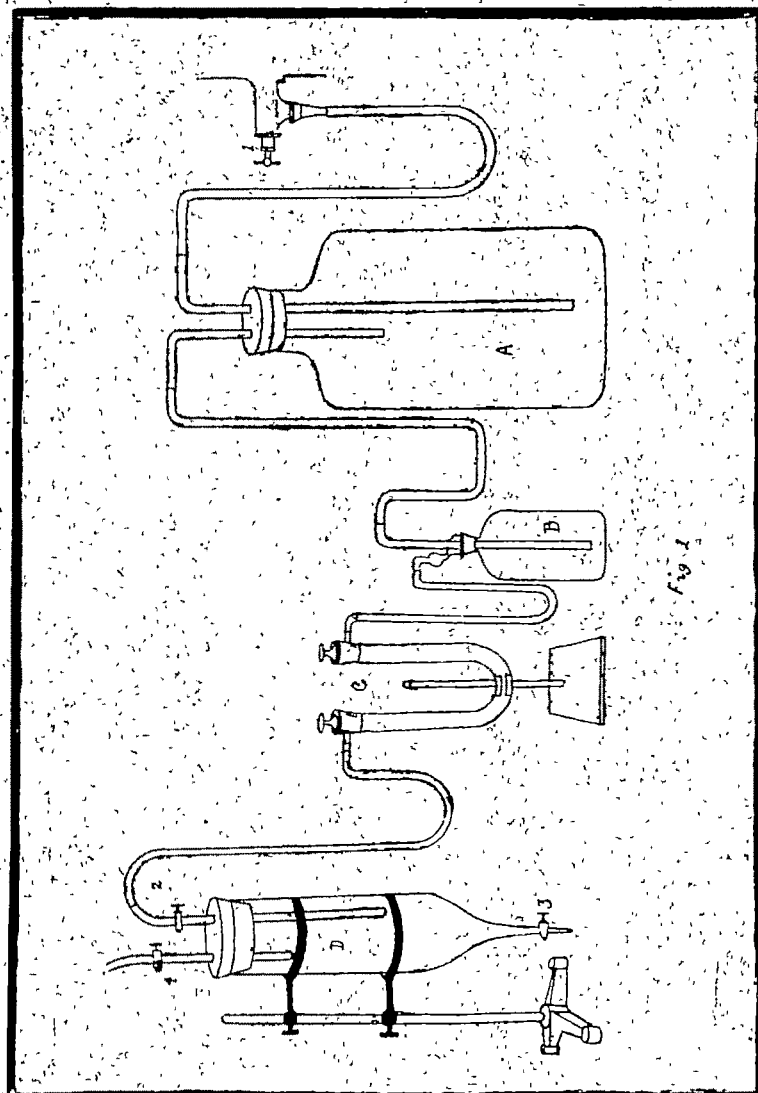
The above compound was obtained as a white amorphous powder, when dry chlorine gas was passed over (7) the corresponding tetraiodo compound. On crystallisation from alcohol it begins to decompose and darken at 100° . Yield quantitative.

(Found: Cl=21.16. $\text{Hg}_2(\text{NO}_3)_2\text{Cl}_4$ requires Cl=21.32 per cent.)

The compound was sparingly soluble in cold water, more in boiling water and freely soluble in alcohol. The halogen could be quantitatively precipitated from its water solution by silver nitrate.

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Surface Tension of Sodium and Potassium Amalgams at the Amalgam-Benzene Interface.

BY

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AND

D. M. MUKERJI.

A systematic study of sodium amalgams containing high percentages of sodium was made by Vanstone who by varying the proportion of sodium and mercury and studying the mixture with respect to thermal diagram (Trans. Faraday Soc., 1911, 7, 42) and electrical conductivity (Trans. Faraday Soc., 1914, 9, 291) found out the exact composition which corresponded to the formation of a definite compound.

Comparatively very little is known about the state of sodium-mercury and potassium-mercury mixtures in the liquid state, when only very small quantities of sodium and potassium are present in the mixtures.

Whilst the solid crystalline amalgams of the alkali and alkaline earth metals are regarded as definite chemical compounds, the corresponding liquid amalgams on the other hand have generally been regarded as mercurial solutions of this metal in the monatomic condition. George McP. Smith (Amer. Chem. J., 1907, 37, 506) does not agree with the latter view and has submitted evidence to show that even in the liquid state chemical compound formation takes place and the liquid amalgam constitutes solution of those salts in mercury. Vanstone (Jour. Chem. Soc., 1914, 105, 2617) and Maey (Zeit. Phy. Chem., 1899, 29, 119) have shown that the specific volume in

amalgams does not suffer any profound change when combination takes place between the metal sodium and mercury.

It was, therefore, considered desirable to examine such other physical properties, as surface tension, viscosity, etc., of amalgams in order to see if evidence could be accumulated for the views put forward by George McP. Smith (*loc. cit.*). These properties have been shown by Padoa [Atti. R. Accad. Lincei, 1914, (V), 23, i, 88—94], Beck (Zeit. Phys. Chem., 1904, 48, 670) and others to undergo marked deviation from the mixture law when compound formation takes place and can be used with advantage to bring to light the behaviour of the mixtures at various concentrations.

The present investigation deals with the determination of the surface tension of sodium and potassium amalgams at the amalgam-benzene interface. To observe the various stages that amalgams undergo on change of concentration, the composition of amalgams has been varied by very small amounts of sodium and potassium.

EXPERIMENTAL.

Preparation of the Amalgam.

The amalgams were prepared by the electrolytic method of T. W. Richards (J. Amer. Chem. Soc., 1922, 44, 601). An electric current of about $4\frac{1}{2}$ amperes was passed through a saturated solution of Merck's pure sodium or potassium carbonate contained in a cell consisting of mercury cathode and an anode of platinum foil for a known interval of time. After passing the current for the required time, the electrodes were removed and the supernatant liquid was quickly poured out. The amalgam was then taken out in a beaker and was thoroughly washed 4 or 5 times with distilled water. Subsequently it was

taken in a separating funnel and after smart agitations, it was transferred to a vessel containing alcohol. The amalgam, after being washed over twice with alcohol to remove traces of water, was transferred to a flask which was evacuated and was heated for some minutes. Having thus dried the amalgam, it was well shaken in the flask and allowed to cool. When cooled, it was transferred to the storing vessel where it was kept out of contact with air. The amalgams of various concentrations were prepared by passing the same current under the same circumstances for varying intervals of time. In this way the sodium amalgams containing 0.033 % to 0.312 % of sodium and potassium amalgams containing 0.056 % to 0.182 % of potassium were prepared.

Storing of the Amalgam.

The amalgam was stored in a vessel A by an arrangement shown in figure 1. The vessel is set in connection with a large reservoir B of nitrogen through a U-tube C containing calcium chloride and a bottle D containing strong sulphuric acid. The amalgam was quickly poured out of the evacuated flask into the vessel A which was soon after fitted with an air-tight rubber stopper. The taps, 1, 2, 3 and 4 were opened and current of dry nitrogen was passed until the whole system was filled with it (nitrogen). As will be shown later, the amalgams, when kept as above, maintained their composition as such for a period of more than a fortnight.

Analysis of the Amalgams.

After rejecting 8 or 10 drops from the storage vessel, about 10 grams of the amalgam were taken in previously weighed weighing-bottles which were reweighed. The amalgam from the weighing-bottles was transferred to flasks to which a small quantity of water was added and

which were kept unexposed to air. The action of water on amalgam appeared to be very vigorous at first but slowed down after a short time. The reaction was allowed to proceed until no evolution of the gas could be noticed even on brisk shaking. The alkali (sodium or potassium hydroxide) formed in the reaction was titrated with standard hydrochloric acid which was prepared nearly of the same strength as the alkali solution.

At first some experiments were performed to see whether the composition of the amalgam remained the same on keeping it for some time in the storing vessel. The results of the above investigation are shown in the following table :—

TABLE I.

Time of standing of the amalgam.	Amount of Na in 100 grams of the amalgam.	No. of estimations.
Immediately after storing ...	0.553 grams.	2
1 day ...	0.554 "	2
2 days ...	0.554 "	4
14 days ...	0.553 "	2
16 days ...	0.553 "	2

It will be seen from the above table that the strength of the amalgam remains constant for all intents and purposes.

By taking fractions of the amalgam from the various parts of the storing vessel, it was also observed that the composition was the same throughout. The above results indicate that the amalgam prepared as above is uniform in composition and does not change by keeping in an atmosphere of an inactive gas like nitrogen.

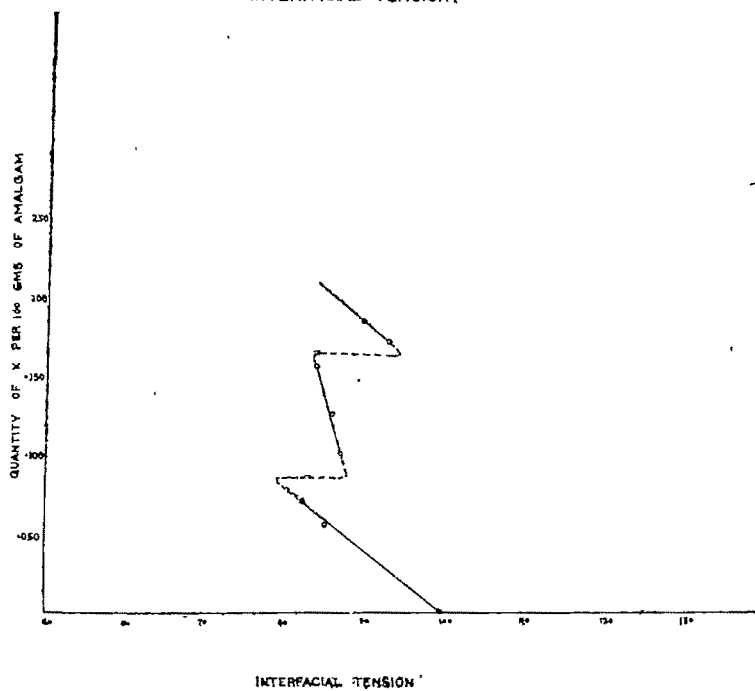
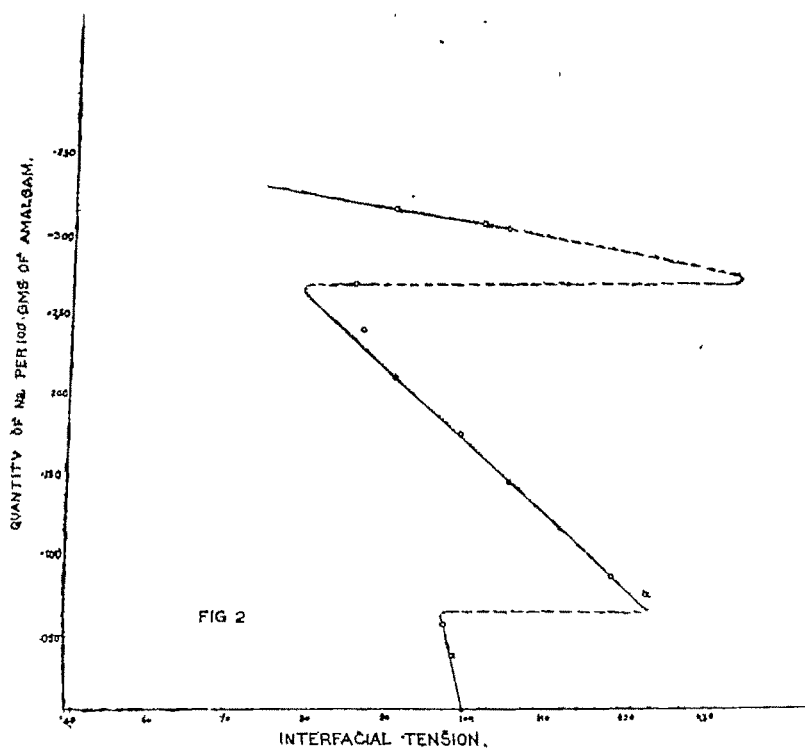


FIG 3

Measurement of the Interfacial Tension.

The interfacial tension between the liquid amalgam and pure benzene was measured by means of a modified form of Donnan's drop-pipette (Zeit Phys. Chem., 1899, 31, 42) used by Bhatnagar and Garner (Journ. Soc. Chem. Ind., 1920, 39, No. 13, 185T). The drop-pipette was kept at a constant temperature of 30° C by enclosing the whole apparatus in an incubator. The dropping-tube was so constricted nearly in the middle that a drop of the liquid amalgam took about 15 seconds to fall. The tip of the dropping-tube was made smooth by grinding it very carefully over a razor-hone and was always kept protected from foreign matter. The amalgam was filled in the bulb by means of capillary filters through the side tube up to a definite mark and was kept protected from air exposure by a small quantity of benzene just sufficient to cover the surface. It was found that benzene does not react appreciably with the amalgam. All necessary precautions were taken to prevent the entrance of dust in the apparatus.

It was shown by Lord Rayleigh [Phil. Mag., 1899, (5), 48, 321] that the surface tension of a liquid can be determined by noting the weight of a drop falling from an orifice of a known diameter. Since then the method has been extended to the measurement of the surface tensions between liquid-liquid surface and liquid-gas surface. \oplus

This method has also been extended to the measurement of relative tensions of solutions of different concentrations. By counting the number of drops in a given volume of a liquid A, whose surface tension is required and a liquid B which is being used for comparison, the relative surface tension of A to B can be calculated from the following relation :—

$$\frac{T_1}{T_2} = \frac{n_2 d_1}{n_1 d_2} \quad \dots (1)$$

where T_1 , d_1 and n_1 are respectively the surface tension, the density and the number of drops of the liquid A in a volume V, and T_2 , d_2 and n_2 are the corresponding quantities for the comparing liquid B.

The tip of the dropping-tube was dipped in benzene contained in a small beaker and the number of drops of the amalgam, n_1 , and the mercury, n_2 , in a given volume were counted. For the sake of greater accuracy, the initial and final coincidence of the level of the liquids in the drop-pipette with the marks were observed through a high-power microscope.

Density of the Amalgam.

The density of the amalgam was measured in benzene by means of a specific gravity bottle. The densities of the amalgams with respect to water were calculated from the density of the benzene which was determined before hand. The values of densities thus obtained are in fair agreement with the values calculated from the specific volume and weights of Maey and Vanstone. The slight deviations which are observable are certainly due to the antiquated and unsatisfactory method used by Maey and Vanstone in preparing these amalgams.

Thus knowing the densities the relative interfacial tensions were calculated from the formula 1.

In the present investigation mercury has been used as a comparing liquid. The values for the interfacial tension of the liquid amalgams have been calculated from the above relative values by assuming the interfacial tension of mercury-benzene to be 100 dynes per cm.

The effect of the increasing quantity of sodium and potassium on the interfacial tension has been brought out in the following tables :—

TABLE II.

Interfacial Tension of Sodium Amalgam at 30°C.

Quantity of Na in 100 gms. of Amalgam.	Drop No.	Density.	$\frac{T_1}{T_2}$	I. T. in dynes per cm.
0.000 gms.	359	13.52	1.00	100
0.033 "	361	13.49	0.99	99
0.053 "	366	13.47	0.98	98
0.072 "	287	13.46	1.24	124
0.084 "	299	13.45	1.19	119
0.143 "	334	13.40	1.06	106
0.172 "	356	13.38	1.00	100
0.207 "	384	13.35	0.92	92
0.238 "	400	13.31	0.88	88
0.266 "	403	13.29	0.87	87
0.299 "	332	13.27	1.06	106
0.302 "	342	13.26	1.03	103
0.312 "	384	13.25	0.92	92

TABLE III.

Interfacial Tension of Potassium Amalgam at 30°C.

Quantity of K in 100 gms. of Amalgam.	Drop No.	Density.	$\frac{T_1}{T_2}$	I. T. in dynes per cm.
0.000 gms.	369	13.52	1.00	100
0.056 "	428	13.47	0.86	86
0.068 "	442	13.46	0.83	83
0.101 "	416	13.43	0.88	88
0.126 "	422	13.41	0.87	87
0.156 "	432	13.39	0.85	85
0.171 "	390	13.37	0.94	94
0.182 "	400	13.36	0.91	91

Discussion of Results.

The results of the above investigation are shown in Tables II and III. The interfacial tension of eleven different sodium amalgams containing from 0.033 to

0.312 gms. per cent. of sodium, and of seven different potassium amalgams, containing from 0.056 to 0.182 gms. per cent. of potassium, has been measured. By plotting the interfacial tensions as abscissa against the concentrations of the alkali metals as ordinates, curves as shown in figures 2 and 3, are obtained.

It will be seen from the curves that the interfacial tension decreases as the concentration is increased from pure mercury to amalgams containing 0.06% of sodium and 0.08% of potassium. A discontinuity occurs at these concentrations which probably corresponds to the formation of compounds of sodium and potassium with mercury.

Again from C to D the interfacial tension decreases on further increasing the quantity of sodium or potassium until a second discontinuity is observed at D. This corresponds to the formation of another compound of sodium and potassium with mercury. The remaining portion of the curves also shows a similar behaviour from E to F.

Hine (J. Amer. Chem. Soc., 1917, 39, 882), while determining the electrical conductivities of sodium, potassium and lithium amalgams, also observed similar discontinuities in the case of sodium. The concentration of sodium in the amalgam at which the resistance begins to decrease almost corresponds to the point D on the curve (figure 2).

It will also be observed from the curves that the relation between the interfacial tension and concentration is linear at all concentrations excepting at points where discontinuity occurs. This is similar to the observations of Dorsey (Phil. Mag., 1897), Srebnitsky (J. Russ. Phys. Chem. Soc., 1912, 44, 145) and of others, namely, that the relation between the surface tension and concentration of solutions is a straight line.

The relation between the interfacial tension and concentration in this case can be expressed by

$$\sigma_A = \sigma(1 - kc)$$

where σ_A is the interfacial tension of the amalgam at the concentration C , σ has the value obtained by producing the curves to the abscissa and K is a constant, which is different for different parts of the curve.

This suggests that compounds of sodium and potassium with mercury are formed in the liquid state even at very low concentration of the alkali metal. At all other concentrations, the amalgam is probably a solution of the compounds and the metal in mercury.

To obtain further evidence of the conclusions already arrived at experiments for the determination of viscosity and other physical properties such as boiling point, etc., of these amalgams are in progress.

The author takes this opportunity of thanking Mr. D. N. Banerji, M.Sc., for the valuable help that he has given in the construction of the apparatus for this investigation.

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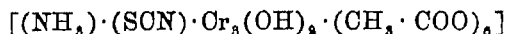
[Received July 7, 1924.]

Complex Chromium Ammonium Compounds

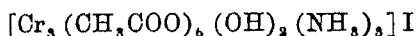
BY

PRIYADARANJAN RAY AND PULIN BEHARI SARKAR.

This paper forms a part of a systematic investigation on the action of ammonium thiosulphate and ammonia upon chromium and cobalt hydroxides. The action of concentrated ammonia and ammonium thiosulphate upon chromium hydroxide has led to the production of two interesting trinuclear chromium ammonium compounds in which the chromium atoms are linked to one another by single bridges through hydroxyl groups. The preparation, description and the establishment of the constitution of these compounds form the subject of the present paper. Examples of trinuclear cobalt compounds with definite constitution are known. But in the case of chromium, though we are familiar with binuclear compounds like rhodochromium and erythrochromium salts, no trinuclear-ammino-compound of definite constitution has yet been described. Werner (Ber., 1908, 41, 3447) and Weinland and Gussmann (Zeit. anorg. Chem., 1910, 67, 167), however, have described a number of compounds with organic fatty acids which contain three chromium atoms in a molecule. A glance at the formulæ of the compounds, namely, monammino-hexacetato-diol-trichromirhodanat

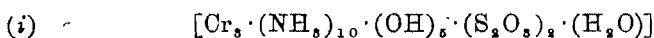


and hexa-acetato-dihydroxy-triammino-trichromi-iodide

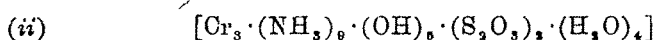


which may be regarded representative of the series, will make it clear. Both the authors have, however, attempted

to clear their constitution, but their views still leave two of the chromium atoms co-ordinatively unsaturated. But these two compounds prepared by the action of ammonium thiosulphate and ammonia upon chromium hydroxide possess the following composition—

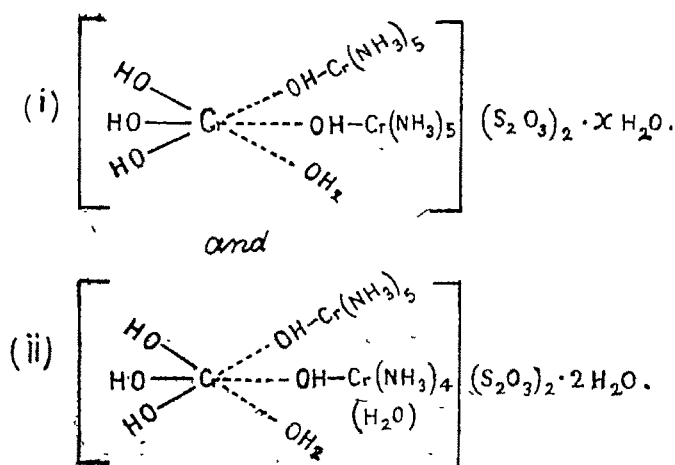


Decammin-monaquo-trihydroxy-diol-trichromium thio-sulphate and



Enneammin-diaquo-trihydroxy-diol-trichromium thiosulphate.

Definite constitution based on Werner's theory can be readily attributed to them; and these have been confirmed by their general behaviour and properties. Their constitutions are represented by the following formulæ:—



Both of them are trinuclear compounds with single bridges. The second is evidently formed from the first by the displacement of one molecule of ammonia by a molecule of water.

EXPERIMENTAL.

Preparation of the decammin-monaquo-trihydroxy-diol-trichromium thiosulphate.—Pure chromium hydroxide prepared from 50 grams of chrome alum was mixed with 50 gms. of ammonium thiosulphate dissolved in a small quantity of water; the mixture was then placed in a strong or pressure bottle and saturated with ammonia gas for several hours till a dark violet solution was obtained and the undissolved chromium hydroxide assumed a violet colour. The mixture was then kept in the dark for some days after which it was filtered. The filtrate was then cooled by ice and treated further with a strong current of ammonia gas. After half an hour or so a dark viscous oily liquid separated out at the bottom. The supernatant solution was then decanted into another flask. The oily liquid was first washed several times with a mixture of alcohol and liquor ammonia (1 : 3) to remove any excess of ammonium thiosulphate, then with absolute alcohol when the oil crystallised completely. The crystals were filtered on the pump at once and washed with absolute alcohol and then in some cases with anhydrous ether. They were dried on the pump by strong suction and removed into weighing bottle at once. The crystals could not be dried in a desiccator as the compound would decompose gradually at atmospheric pressure with loss of ammonia; nor was it found possible to dry the crystals in an atmosphere of dry ammonia.

From the mother liquor another crop was obtained by the careful addition of alcohol, an oil separated out which was washed, crystallised and treated as described above. The final mother liquor on exposure to air for a day or two slowly gave a deposit consisting mostly of violet chromium hydroxide mixed with ammonia and a little ammonium thiosulphate. The yield amounted to only 2-2.5 gms.

Properties.—The crystals were reddish violet, very unstable, readily losing ammonia, extremely hygroscopic and turned into oily liquid by the absorption of moisture. With water a dark oil was formed which slowly passed into a violet-coloured solution and decomposed readily with precipitation of chromium hydroxide. It dissolved slowly in strong ammonia to a clear solution and was decomposed readily by caustic alkalis with evolution of ammonia and separation of chromium hydroxide. With dilute acids sulphur dioxide was evolved and sulphur was precipitated. The substance itself was basic to litmus. With moist silver oxide and water the whole of the thiosulphate was removed and the filtrate was strongly basic. Barium chloride solution also removed the whole of the thiosulphate as barium thiosulphate and a violet solution of the corresponding chloride, which was fairly stable, was obtained. This solution was basic to litmus and gave the following reactions.

1. Potassium ferrocyanide solution gave at first a flocculent and then a light blue-violet crystalline precipitate.

2. Potassium ferricyanide solution gave at first a flocculent and then a crystalline pink-coloured precipitate.

3. Mercuric chloride solution gave a light violet-blue flocculent precipitate.

4. Potassium chromate, after the removal of barium by ammonium sulphate, gave no precipitate but potassium dichromate gave a yellowish brown precipitate.

5. Solid potassium iodide gave a light blue gelatinous precipitate.

6. On evaporation with concentrated hydrochloric acid chromic chloride was formed in solution and the characteristic red-violet crystals of chloropentammin chloride separated out.

Results of analysis:—

I. Sample precipitated by alcohol.

0.4832 gm.	gave 0.1277 gm. of Cr_2O_3 ,	Cr=18.11%
„ „ „	0.5214 gm. of BaSO_4 ,	S=14.81%
		or $\text{S}_2\text{O}_3=25.92\%$
0.3596 „ „	0.0697 gm. of NH_3 ,	$\text{NH}_3=19.37\%$
Hence	Cr : S_2O_3 : $\text{NH}_3=3:2:10$.	

II. Sample precipitated by continuous passage of ammonia,

0.1458 gm.	gave 0.0422 gm. of Cr_2O_3 ,	Cr=19.8%
„ „ „	0.1653 gm. of BaSO_4 ,	S=15.63%
		or $\text{S}_2\text{O}_3=27.35\%$
0.0904 gm. „	0.0190 gm. of NH_3 ,	$\text{NH}_3=21.0\%$
Hence	Cr : S_2O_3 : $\text{NH}_3=3:2:10$	

III. Sample precipitated by 30% alcoholic ammonia from the mother liquor of sample II and washed finally with anhydrous ether.

0.2556 gm.	gave 0.0805 gm. of Cr_2O_3 ,	Cr=21.55%
„ „ „	0.3500 gm. of BaSO_4 ,	S=18.8%
		or $\text{S}_2\text{O}_3=32.9\%$
0.2671 gm. „	0.06207 „ of NH_3 ,	$\text{NH}_3=23.24\%$
Hence	Cr : S_2O_3 : $\text{NH}_3=3:2:10$.	

The atomic ratio in all these samples is, therefore, quite constant, the percentage amount only varied due to the change in the extent of hydration.

Constitution.—As the salt decomposed readily in contact with water no conductivity measurement was possible. The action of silver oxide and barium chloride indicated that both the thiosulphate radicles were in the outer zone. The action of concentrated hydrochloric acid indicated the presence of pentammine. In the light of these facts the compound should be represented by the constitutional formula No. (i), page 92.

obtained by decomposition with barium chloride decomposed slowly in light giving precipitates of chromium hydroxide. A freshly prepared solution obtained by decomposition with barium chloride gave the following reactions :—

1. Potassium ferrocyanide solution gave at first a flocculent then a very light pink crystalline precipitate.

2. Potassium ferricyanide solution gave on warming a dull brown precipitate.

3. Mercuric chloride solution gave a voluminous pink precipitate.

4. Potassium chromate solution, after the removal of barium with ammonium sulphate, gave no precipitate while potassium dichromate gave a light brown crystalline precipitate.

5. Solid potassium iodide gave a heavy pink crystalline precipitate.

Analysis and Composition.

1. 0.1474 gm. of the substance gave 0.0501 gm. of Cr_2O_3 :
Cr=23.2%

“ “ “ “ 0.2057 gm. of BaSO_4 ,
S=19.1%

0.0570 “ “ “ 0.0130 gm. of NH_3 ,
 NH_3 =22.75%

0.0924 “ “ “ 0.0202 gm. of NH_3 ,
 NH_3 =21.87%

II. 0.2344 gm. of the substance gave 0.0794 gm. of Cr_2O_3 ,
Cr=23.00%

“ “ “ “ 0.3163 gm. of BaSO_4 ,
S=18.55%

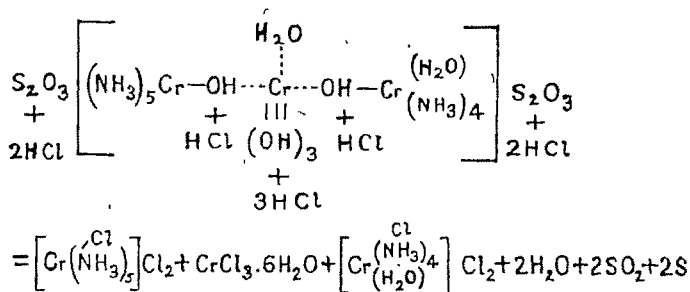
$[\text{Cr}_2(\text{NH}_3)_6(\text{OH})_2(\text{S}_2\text{O}_8)_2(\text{H}_2\text{O})_4]$ requires

Cr=22.75%, S=18.66%, NH_3 =22.3% per cent.

Constitution.—The substance was basic to litmus hence it was inferred to be a hydroxo compound. The action of strong hydrochloric acid indicated that it contained a

pentammine group. In its general behaviour with other reagents it resembled the first compound in many respects. Hence its constitution should be represented in a similar way as the first. The constitutional formula No. (ii), page 92 has therefore been adopted.

The action of hydrochloric acid can, therefore, be represented as follows:—



decomposes by heat into

CrCl_3 , NH_3 and H_2O .

From the method of formation and the properties of these compounds it appears that in the beginning the first compound is formed in the violet solution obtained by the action of ammonia and ammonium thiosulphate upon the chromium hydroxide. This is precipitated out of the solution by the passage of ammonia or by the addition of alcohol, in the form of an oil. This substance is rather unstable. On the other hand the second compound is quite stable in the dry state and is obtained as well-defined heavy crystals when the violet solution is kept in contact with chromium hydroxide for several months. The first compound is, therefore, gradually changed into the more stable second compound by the conversion of one pentammine residue into an aquotetrammine one.

As the compounds are either almost insoluble or unstable in water, their constitution could not be confirmed by physical methods.

Our best thanks are due to Prof. Sir P. C. Ray for the kind interest he has taken in the work.

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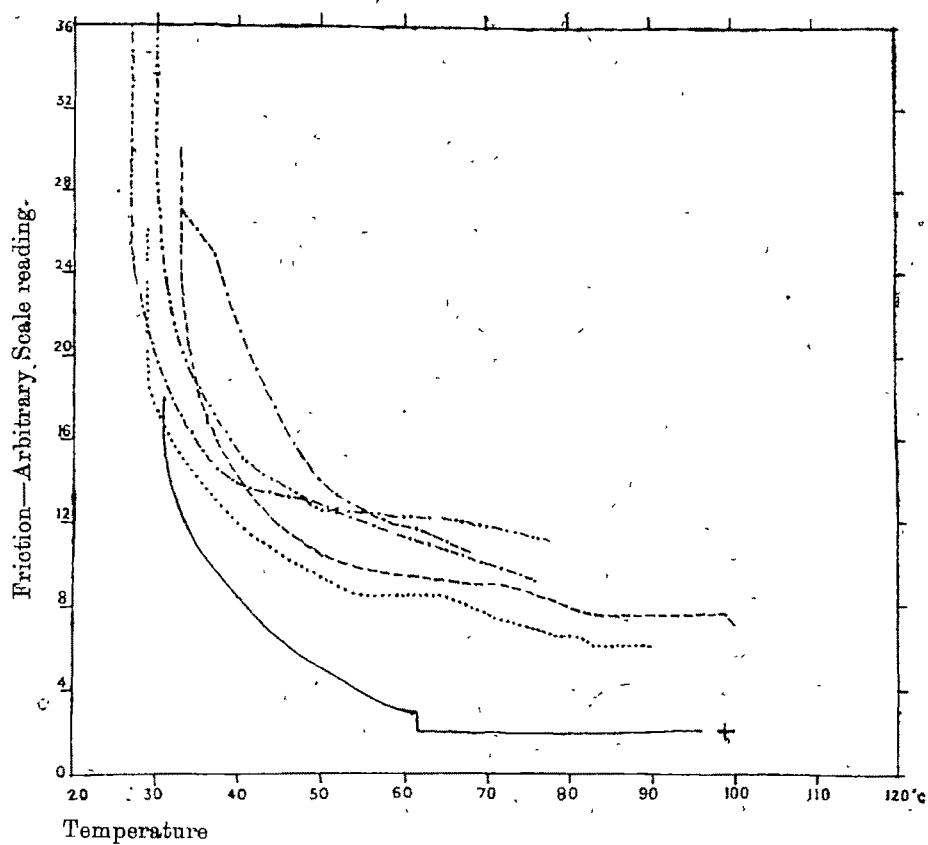


DIAGRAM 1.—MOBIL OIL B.

Friction in lbs. per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

————	at 10 lbs. pressure per sq. inch.
.....	" 20 " " " "
— — — —	" 30 " " " "
— . — .	" 40 " " " "
— . . —	" 50 " " " "
— — — —	" 60 " " " "

Friction Tests on Oils for use on Motor-car Engines.

BY

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These tests were undertaken to see whether a cheaper oil could not be used as a substitute for the expensive motor-car engine oils now on the market. It was first of all necessary to ascertain what laboratory tests a satisfactory oil must answer. It was decided to test a variety of oils, including some well-known motor-car oils and some cheaper oils such as cylinder oils, engine oils, spindle oils and castor oil, on a friction-testing machine at temperatures up to 100° or 120°C under moderate pressures (up to 60 lbs. per sq. in.) as it was thought these were about the conditions under which an oil had to operate in lubricating the walls of motor-car engine cylinders. It was expected that some oils would not be able to prevent solid friction at these high temperatures and such oils would have to be discarded as unsuitable for the purpose under consideration. Of those oils which could prevent solid friction the best would be those which had the lowest friction co-efficient both at this high temperature and also at lower temperatures. A small Thurston's friction-testing machine was used and

the following families of curves may be taken as typical of the results obtained:—

1. Mobiloil B (Vacuum Oil Co.).
2. Motor Oil B (Burmah Oil Co.).
3. Castor oil.
4. Standard Gas Engine Oil (Standard Oil Co.).
5. Cylinder Oil No. 660 (Burmah Oil Co.).
6. Red Engine Oil No. 2 (Standard Oil Co.).
7. Spindle Oil No. 40 (Burmah Oil Co.).

These curves were all obtained at a speed of 1,000 to 2,000 revolutions per minute and generally between 1,700 and 2,000. Friction was found to be practically independent of speed under the conditions of these experiments.

These tests were all carried to as high a temperature as possible and the ends of the curves on the high temperature side indicate the maximum temperatures at which the oils were able to prevent solid friction. (There are a few exceptions where solid friction did not set in even at the highest temperatures attained. In these cases a + sign is placed at the end of the curve.) When solid friction set in the co-efficient of friction began to rise very rapidly and Diagram 8 (Castrol T at 30 lbs. pressure) may be taken as typical of the curves obtained. In the above families (Diagrams 1—7) all the curves have been cut short just where the friction began to rise. In the small testing machine which we used there is no means of replacing the oil which works out of the bearing so the machine was stopped as soon as solid friction set in, a fresh quantity of oil applied to the bearing and running resumed as quickly as possible. In all cases the normal curves (friction decreasing with rise of temperature) were carried as far as possible by renewing the oil. The information obtained as regards limiting temperatures, *i.e.*, the maximum temperatures at which the oils could

prevent solid friction, is summarised in Diagram 9 which gives the limiting temperatures under different pressures for the various oils examined. (A curious feature is that many oils would not stand such a high temperature at intermediate pressures as they would at higher pressures.) Judging from the maximum temperatures at which an oil can be used without solid friction setting in, the order of merit for the oils examined is:—

Castor Oil	will stand up to 90°C
B. O. C. cylinder oil No. 660	" " " "
Castrol T	" " " "
Castrol R (if anomalous behaviour at 50 lbs. can be overlooked)	" " " "
Mobiloil B	" " " 70°C
Standard gas engine oil	" " " 60°C
Castrol F	" " " 50°C
B. O. C. Motor Oil B	" " " 50°C
Red Engine Oil	" " " 40°C
Spindle Oil B. O. C. no. 40	" " " 30°C

But we must also take into account friction at ordinary temperature because an oil with a high friction at ordinary temperatures would make an engine very difficult to start. If we assume that any oil showing a friction higher than 5 lbs. per sq. inch at 30°C under any pressure up to 60 lbs. per sq. inch is unsatisfactory, this rules out Castor Oil, B. O. C. Cylinder Oil No. 660, and Castrol R and leaves the order of merit

Castrol T.
 Mobiloil B.
 Standard Gas Engine Oil.
 Castrol F.
 B. O. C. Motor Oil B.
 Red Engine Oil.
 Spindle Oil.

If the oil will perform the required function at all the

less friction it gives the better. This consideration gives a slight preference to Castrol T.

As a conclusion from these considerations it will be seen that the oils on the market as motor-car engine oils answer the tests better than the other oils examined, such as castor oil, cylinder, engine and spindle oils. The only other oil examined which answered the tests was Standard Gas Engine Oil.

But these experiments showed us that the temperature at which solid friction occurs depends a great deal on the supply of oil. With a more efficient system for continuously supplying oil to the moving parts the maximum temperature attainable without solid friction can be increased. We may assume that if used with a better arrangement for oil supply the order of merit would remain the same; but this is an assumption which may or may not be justified. Trying to test this point we had a couple of oil tubes bored through the upper brass of the small Thurston's machine and had these fitted with oil cups. This was an imperfect arrangement and the thinner oils flowed through the bearing so quickly that it was difficult to keep the cups filled and a large quantity of oil was used for each test. We find from Archbutt and Dealey's book on lubricants that friction-testing machines with more efficient oil supply have been designed and would be more suitable for these tests. However, with the apparatus at our disposal we arrived at the interesting conclusion that even the lightest oil in our selection, *viz.*, Spindle Oil B. O. C. No. 40, could be used up to 100°C without solid friction setting in (diagram 10). Moreover on our modified machine Spindle Oil gave a more satisfactory test than Castrol T; and of course if there was no danger of solid friction the lighter oil would be preferable to the heavier as its co-efficient of liquid friction is less. All appears to depend, then, on the

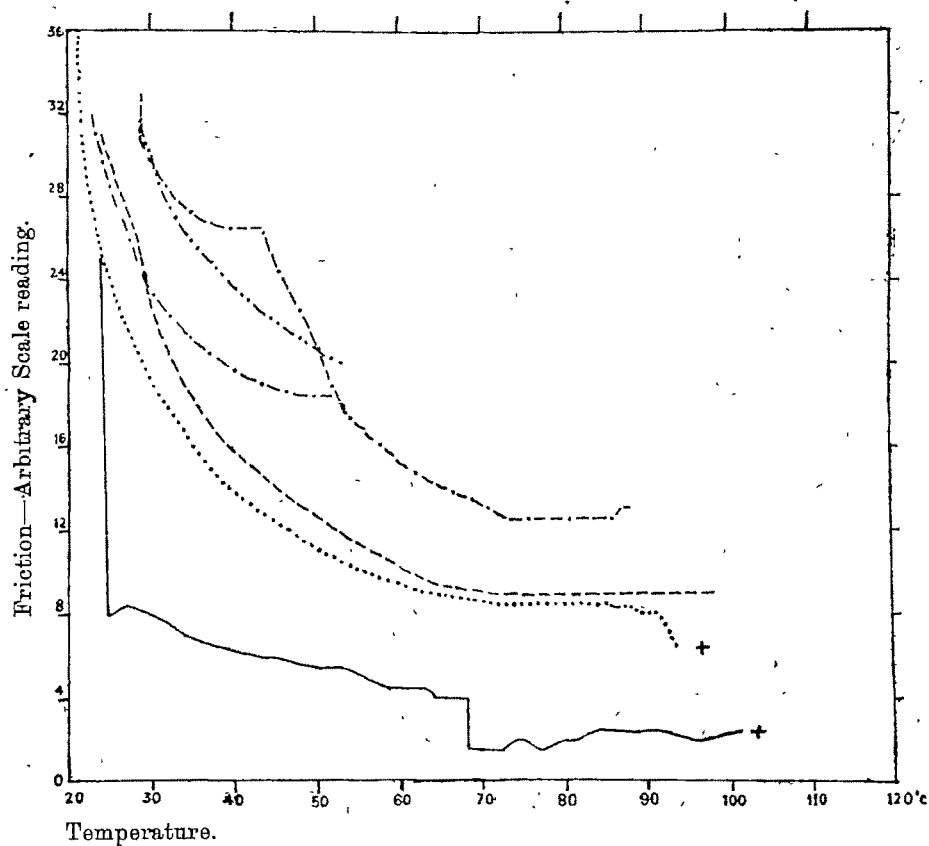


DIAGRAM 2.—MOTOR OIL B.

Friction in lbs. per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

—————	at 10 lbs. pressure per sq. inch.				
.....	" 20 "	"	"	"	"
— — — —	" 30 "	"	"	"	"
—	" 40 "	"	"	"	"
— . . . —	" 50 "	"	"	"	"
————	" 60 "	"	"	"	"

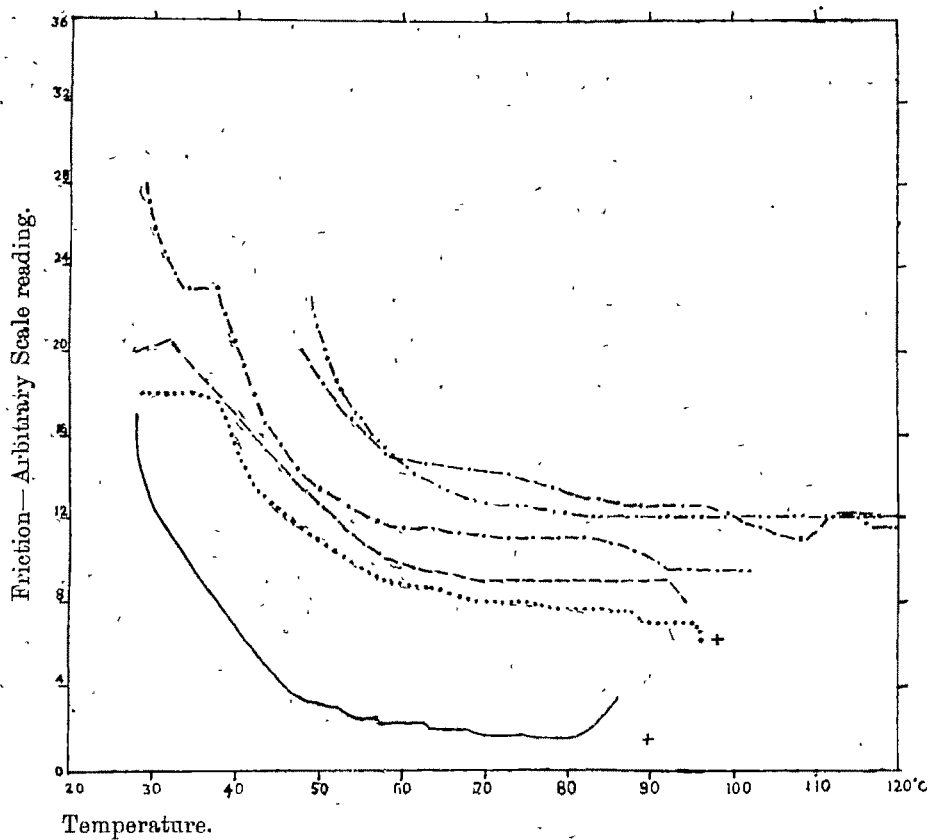


DIAGRAM 3.—CASTOR OIL.

Friction in lbs. per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

————	at 10 lbs. pressure per sq. inch.
.....	" 20 " " " "
— — —	" 30 " " " "
— . —	" 40 " " " "
— . . —	" 50 " " " "
— — —	" 60 " " " "

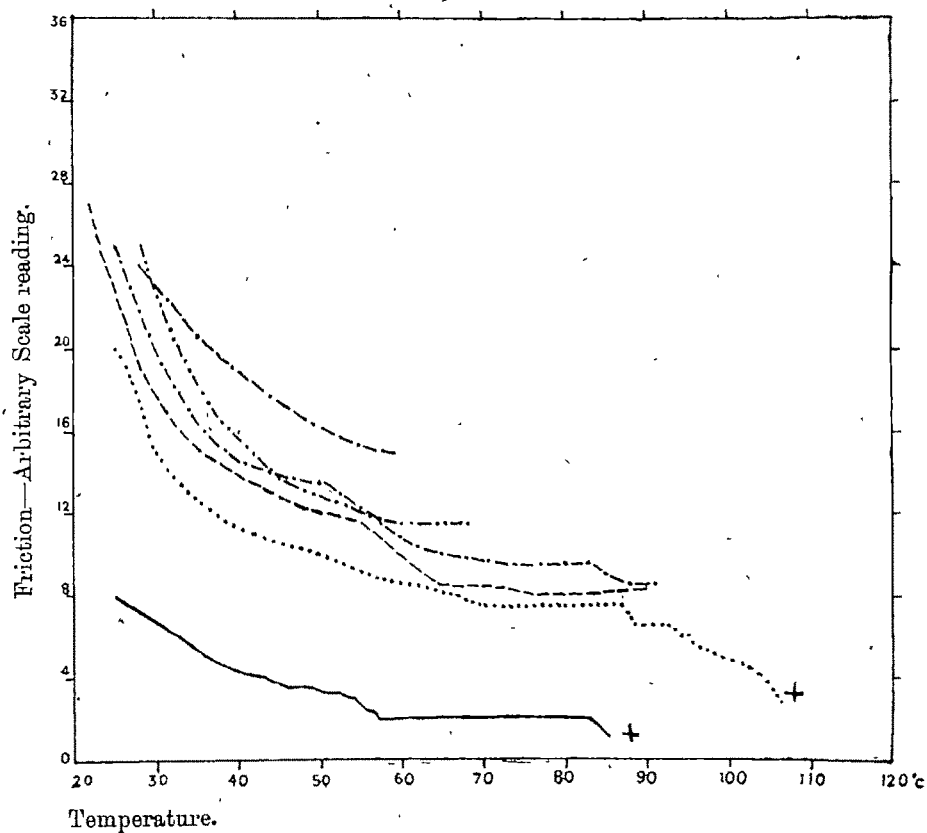


DIAGRAM 4.—STANDARD GAS ENGINE OIL.

Friction in lbs. per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

— at 10 lbs. pressure per sq. inch.

.....	"	20	"	"	"	"	"	"
— — — —	"	30	"	"	"	"	"	"
—	"	40	"	"	"	"	"	"
—	"	50	"	"	"	"	"	"
—	"	60	"	"	"	"	"	"

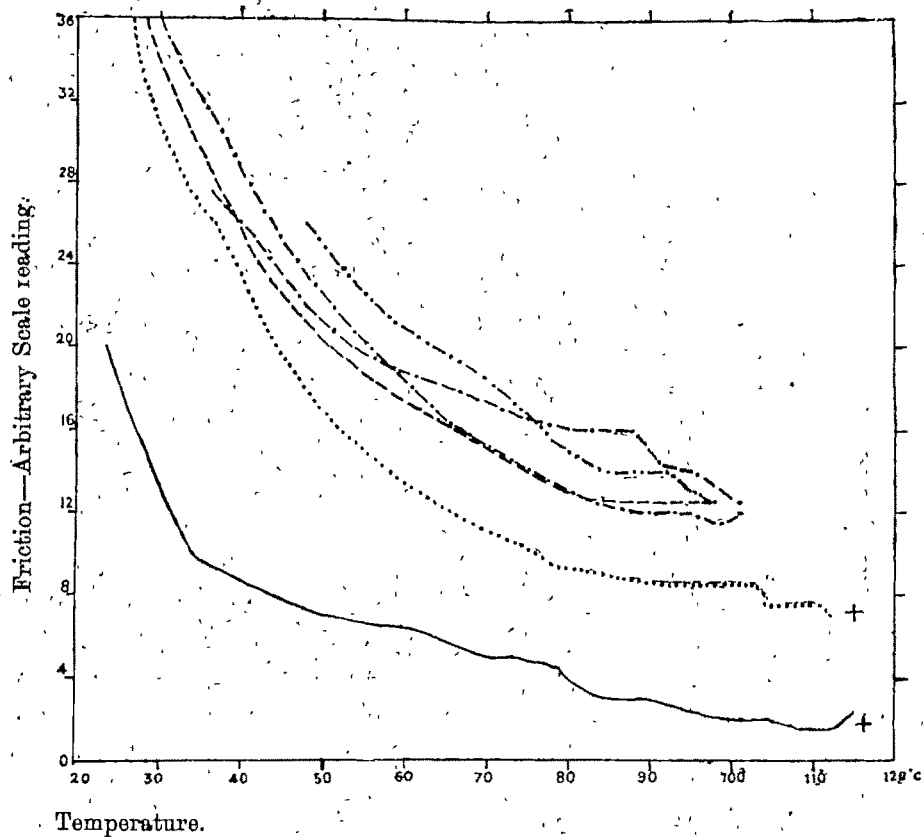


DIAGRAM 5.—CYLINDER OIL No. 660.

Friction in lbs. per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

———— at 10 lbs. pressure per-sq. inch.

..... " 20 " " " " "

— — — " 30 " " " " "

— — — " 40 " " " " "

— — — " 50 " " " " "

— — — " 60 " " " " "

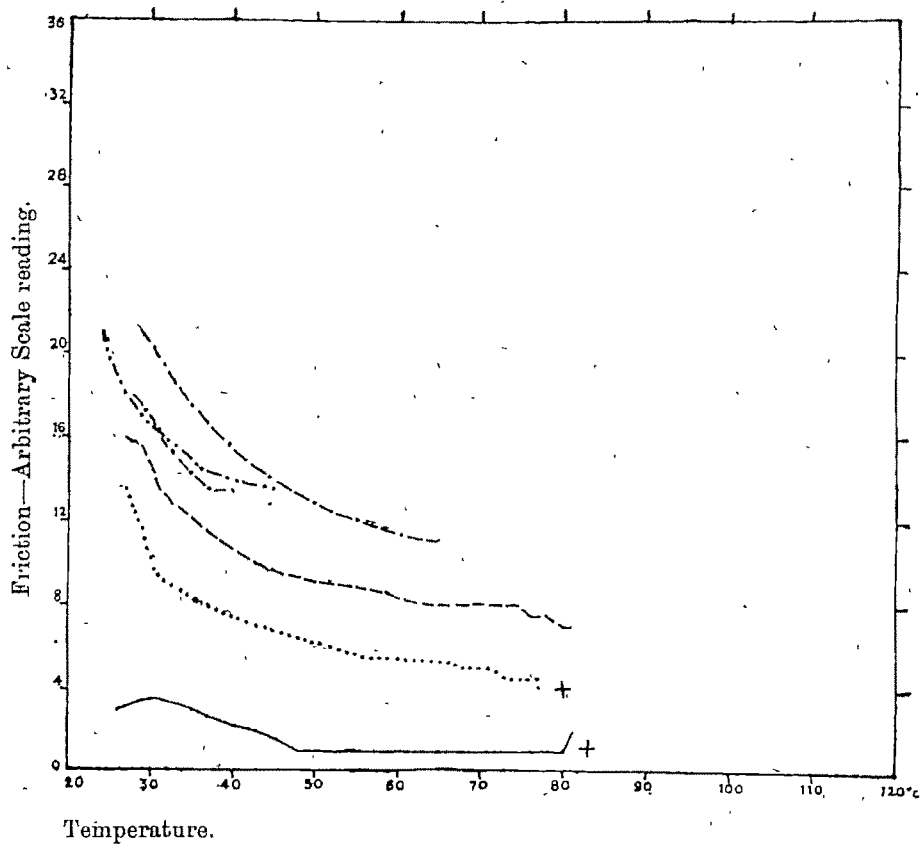


DIAGRAM 6.—RED ENGINE OIL No. 2.

Friction in lbs. per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

————	at 10 lbs. pressure per sq. inch.
.....	" 20 " " " "
— — — —	" 30 " " " "
— * — *	" 40 " " " "
— . . — .	" 50 " " " "
— — — —	" 60 " " " "

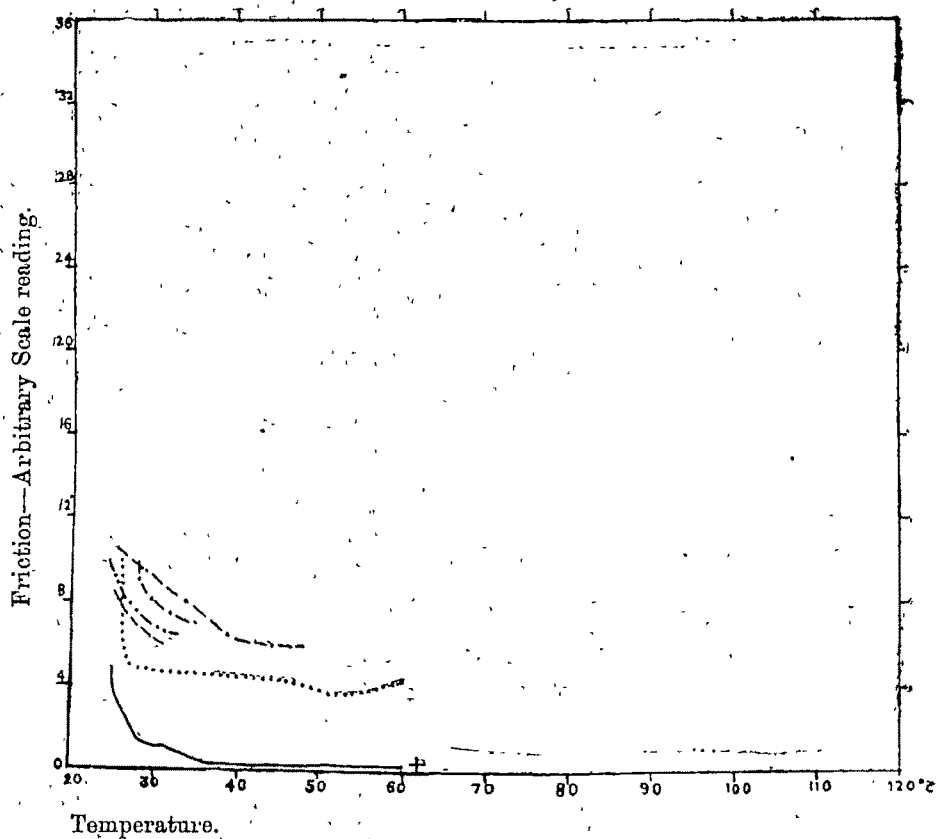


DIAGRAM 7.—SPINDLE OIL NO. 40.

Friction in lbs. per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

———— at 10 lbs. pressure per sq. inch.

.....	"	20	"	"	"	"	"
-----	"	30	"	"	"	"	"
- - - - -	"	40	"	"	"	"	"
- . - . -	"	50	"	"	"	"	"
- - - - -	"	60	"	"	"	"	"

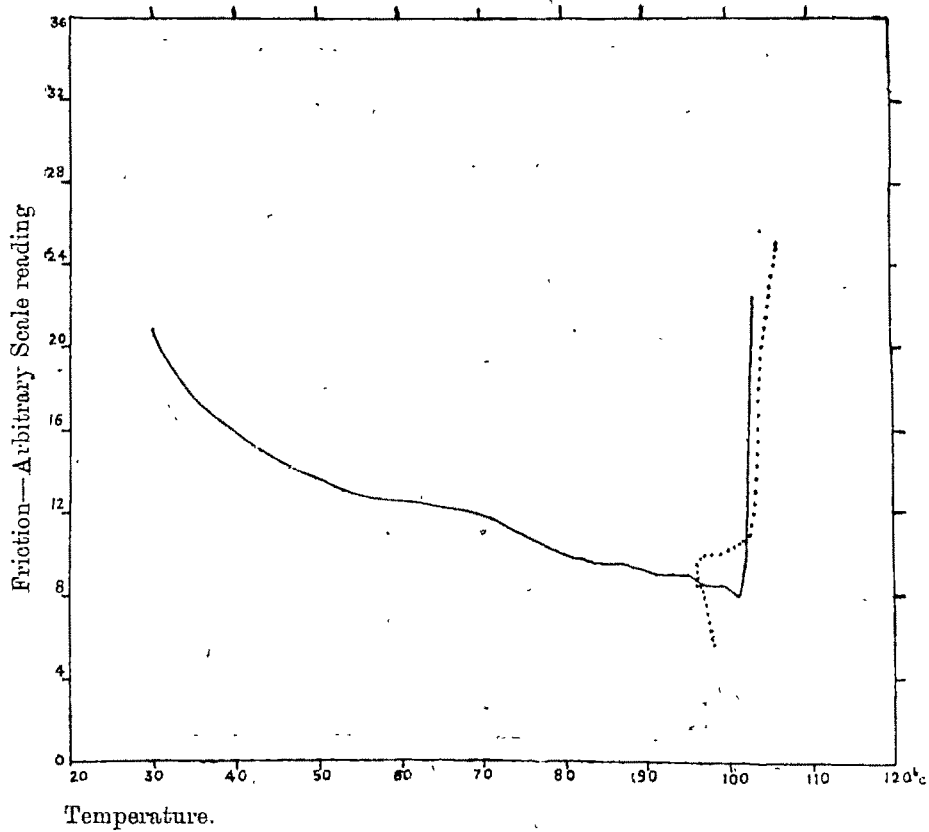


DIAGRAM 8.—CASTROL T.

(At 30 lbs. pressure per sq. inch.)

Friction in lbs. per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

— with 1st supply of oil.

..... „ 2nd „ „

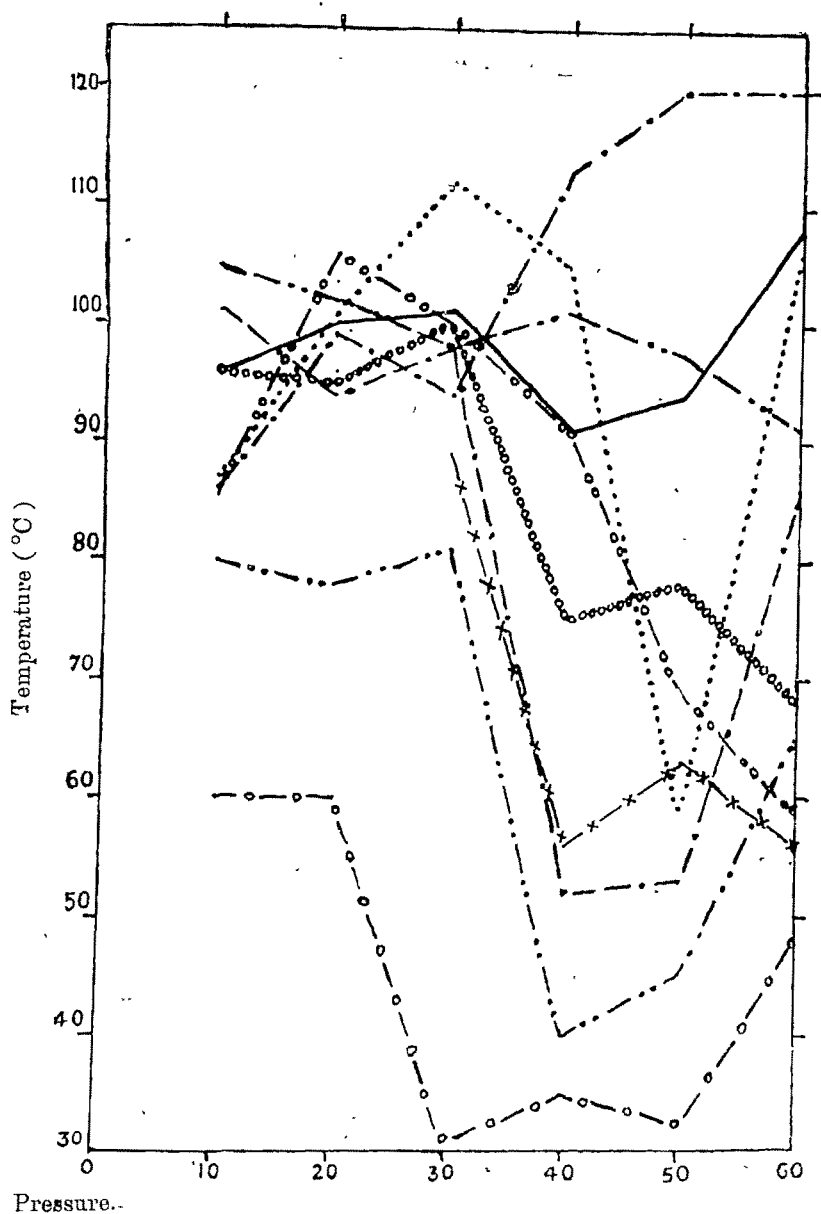


DIAGRAM 9.—LIMITING TEMPERATURE—PRESSURE CURVES.

—	stands for Castrol T	— o o	stands for Standard Gas Engine Oil
.....	" " Castrol R	—	" " Cylinder Oil No. 660
o o o o o	" " Mobil Oil B	— . . .	" " Red Engine Oil No. 2
— — .	" " Motor Oil B	— o —	" " Spindle Oil No. 40
— . — .	" " Castor Oil	— x —	" " Castrol F

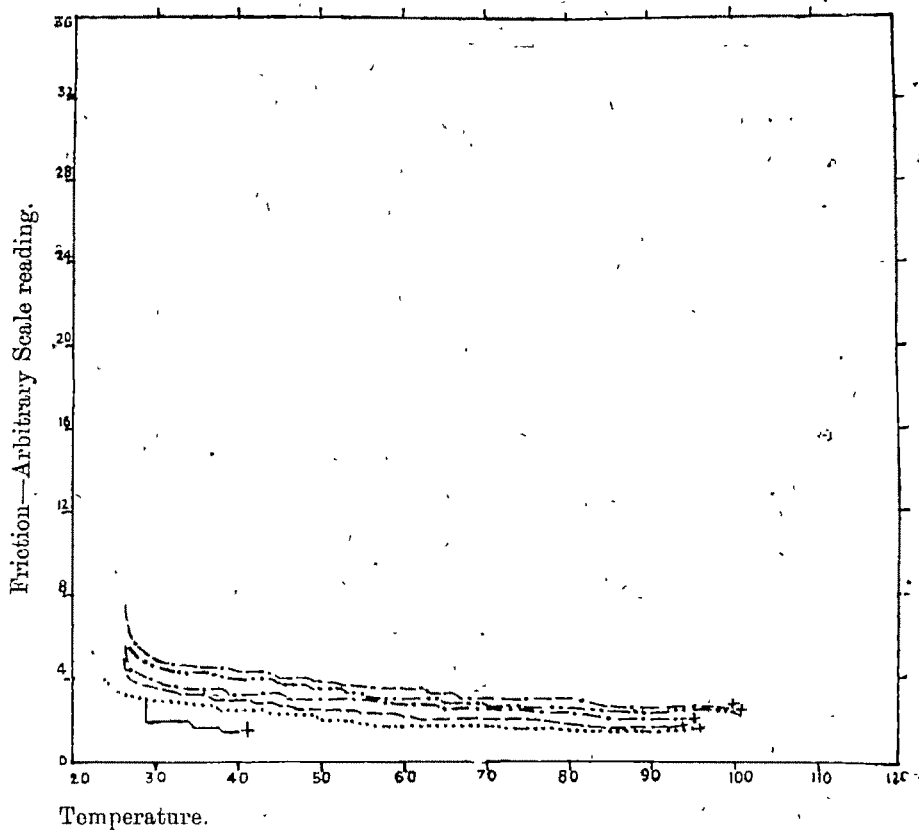


DIAGRAM 10.—SPINDLE OIL No. 40.

(Tested on modified friction-testing machine.)

Friction in lbs per sq. inch of bearing surface = Arbitrary Scale reading $\times 0.127$

————	at 10 lbs. pressure per sq. inch.
.....	" 20 " " " "
— — — —	" 30 " " " "
- . - . - .	" 40 " " " "
- . . - -	" 50 " " " "
— — — —	" 60 " " " "

efficiency of the mechanical arrangements for the supply of oil to the moving parts of the motor-car engine. With an inefficient system the motor-car engine oils on the market are the best to use, but with a more perfect system it should be possible to use a lighter oil and get a much better mileage from the fuel owing to decreased friction.

The Spindle Oil was tried in a Dodge car but after a few miles the white metal was burnt out from one of the big-end bearings. In this car there is a combination pump and splash feed oiling system and it is not known whether the oil failed because it was too thin for the pump to circulate it properly or whether the pressure on the big end bearing was too great for such a thin oil. There was no obvious trouble as regards the lubrication of the cylinder walls and it may be that we have exaggerated the importance of this part of motor-car engine lubrication. Obviously the only safe way to arrive at a conclusion as to the relative merits of different motor-car engine lubricants is to test them thoroughly in a motor-car engine, or, preferably in a number of engines with different lubricating systems. Nevertheless it was thought that our laboratory experiments were sufficiently interesting to be put on record.

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The Reactivity of the Methylene Group in Coumarin-4-acetic Acids and their Esters.

Condensation with Salicylaldehyde to 4:3'-Dicoumaryls.

BY

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AND

KARNAD KRISHNA ROW.

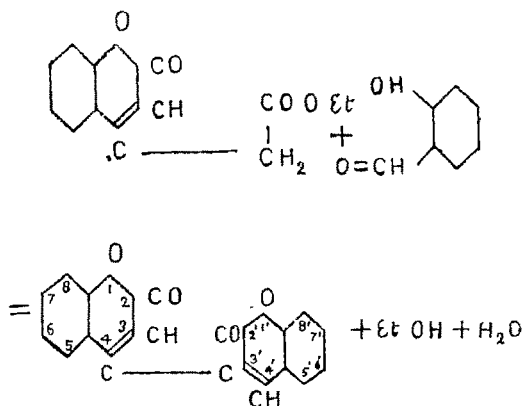
Sometime ago it was observed by one of us that the ethyl ester of 7-methyl-coumarin-4-acetic acid (Fries and Volk, *Annalen*, 1911, 379, 107) readily formed a yellow monosodium derivative when treated with metallic sodium (wire) in dry solvents like ether or benzene in the cold. It was quickly hydrolysed by cold water regenerating the original ester and behaved in other respects like the sodium derivatives of phenylacetic and cyanacetic esters, showing clearly that it was formed by the replacement of one of the hydrogen atoms of the methylene group by metallic sodium. This observation which was repeated in the cases of other coumarin- and naphthapyrone-acetic esters made it obviously desirable to study the reactivity of the methylene group in these bodies as a class and to compare them with the phenylacetic esters to which they bear a close resemblance in structure. In the present communication we have studied only one particular example of this reactivity, *viz.*, their property of condensing with salicylaldehyde. The reaction between phenylacetic acid or its ethyl ester and salicylaldehyde has been the subject of several investigations (Oglialozo,

Gazetta, 1879, 9, 428; Frank and Kostanecki, Ber., 1905, 38, 939, etc.). A few preliminary experiments relating to the determination of the most favourable conditions under which this reaction took place led to results which are not perhaps without significance in their bearing on the relative influence of the benzene and the pyrone rings upon the reactivity of the $\text{CH}_2\text{-COOH}$ group attached to them. It was found that in the case of phenylacetic acid the best results were uniformly obtained by working under the conditions of Perkin's reaction, *i.e.*, by heating the free acid and the aldehyde with sodium acetate and acetic anhydride, whilst if the ethyl ester of the acid be employed and the experiment carried out under the conditions of Knoevenagel's reaction, no condensation took place at the ordinary temperature and it was only after continuous boiling for 10 to 12 hours that a very small amount of the 3-phenyl-coumarin could be isolated. The coumarin-acetic acids, on the other hand, were found to condense almost quantitatively when an alcoholic solution of their ethyl esters was warmed for a short time with the aldehyde in the presence of a few drops of piperidine (Knoevenagel); the free acids also reacted either by Perkin or Knoevenagel's methods, although the yields of the product were somewhat poorer. These experiments, therefore, would lead one to the conclusion that the reactivity of the methylene group in coumarin-acetic esters is greater than that of this group in phenylacetic esters at least so far as their power of condensing with salicylaldehyde is concerned, although in the case of the free acids, the difference, if any, is hardly appreciable.

In the course of this work an unexpected irregularity was found to present itself in connection with the condensation of substances in which either of the reactants contained more than one hydroxyl group in their molecules. Thus, whilst 7-hydroxy-coumarin-4-acetic ester reacted

smoothly with salicylaldehyde in the presence of piperidine, the 7:8-dihydroxy-coumarinacetic ester failed to give any condensation product at all under the same conditions. Similarly, resorcylic aldehyde could not be made to undergo condensation with any of the coumarin-acetic esters by Knoevenagel's reaction. It should be mentioned, however, that in both these cases condensation was brought about without much difficulty under the conditions of Perkin's reaction.

The compounds described in this paper have been termed 4:3'-dicoumaryls, the condensation of salicylaldehyde with the coumarinacetic esters taking place in the following manner:



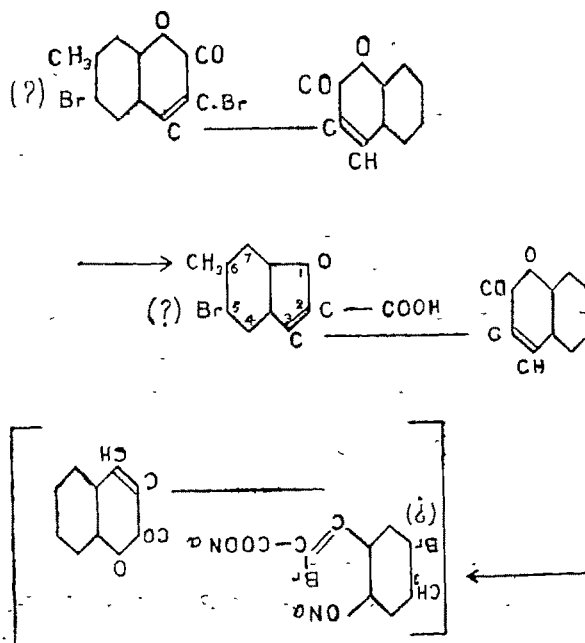
The only compound of a similar type to which reference is found in literature is a 3:3'-dicoumaryl prepared by heating salicylaldehyde with sodium succinate and acetic anhydride in a sealed tube at 140° for forty hours (Dyson, *Trans.* 1887, 51, 62; also Fittig, *Annalen*, 1889, 255, 1).

This dicoumaryl is described by Dyson as a light yellow crystalline powder insoluble in the ordinary organic solvents, and not fusing when heated up to 330°C; these properties are shared to a large extent by the

4: 3'-dicoumaryls which are usually coloured, have high melting points, and dissolve very sparingly in alcohol, acetic acid, benzene, etc., the most convenient medium for their crystallisation being nitrobenzene diluted with acetic acid or alcohol. Boiling alkalis dissolve them only slowly, acids precipitating the unchanged dicoumaryls; if however, the acidification be carried out at a low temperature, unstable acids are first precipitated in the manner of the coumarinic acids which dissolve completely in cold sodium carbonate but lose their property on standing for some time being changed into the original substances. They could not be made to combine with sodium bisulphite, a result which is in accord with the observation previously made (Dey and Row, *Trans.*, 1924, 125, 554) that the presence of an alkyl group—the coumaryl group in the present instance—in either the 3- or the 4-position hinders the formation of additive compounds.

The bromination of these dicoumaryls has also been studied in one case. The introduction of the halogen can be carried out under the usual conditions, although it is found difficult to restrict its entrance into only one position in the molecule. Thus, on treating 7-methyl-4: 3'-dicoumaryl with an amount of bromine calculated for the introduction of only one atom of the halogen, the product that was obtained, was found to be largely a mixture of a dibromo-derivative, a probable mono-bromo-derivative which could not be purified, and some unchanged material. The dibromo-compound could be readily prepared by boiling in glacial acetic acid with a slight excess over the required proportions of bromine. One of the bromine atoms was proved to have occupied the 3-position that remained free in the molecule, as it was split off on boiling with alcoholic potash with the formation of a 3'-coumaryl-3-benzfuran-2-carboxylic acid

derivative, thus :



The position of the second bromine atom has not been definitely established, though from analogy it may be assumed to have attached itself to the 6-position in the coumarin ring containing the methyl group.

The other chloro-, bromo- and nitro-dicoumaryls described in this paper have been prepared by the synthetic method, *i.e.*, by condensation of the coumarin-acetic esters with the halogenated or nitrosalicylaldehydes, the positions of the substituents being thereby fixed.

EXPERIMENTAL

The coumarin-4-acetic acids employed in this investigation have been prepared by a modified method directly from citric acid so as to avoid the rather troublesome process of isolating the intermediate acetone dicarboxylic

acid. After several trials, the following conditions were found to be the most suitable for ensuring a satisfactory yield by this reaction :

Citric acid (24 grams) and concentrated sulphuric acid (32 c.c.) were mixed in a capacious flask and shaken for half an hour, and the mixture then slowly warmed on a large water bath to a temperature of 70°C , the thermometer dipping in the mixture. Carbon monoxide was copiously given off and the mixture left at this temperature for 10 to 15 minutes. As soon as the evolution of gas slackened, the flask was removed from the bath, allowed to stand for about 5 minutes till the liquid became clear and free from gas bubbles, and then cooled in ice. The phenol or naphthol (1/10 mol.), and a further amount of strong sulphuric acid (14 c.c.) were now gradually added, and the mixture shaken, taking care not to allow the temperature to rise above 10° . The dark-coloured semi-solid mass was left in the ice chamber overnight, and then poured into excess of cold water when usually a bulky precipitate of a yellow to brown colour separated out. The precipitate was digested with N/10 sodium carbonate solution (about a litre) for 10 minutes on a boiling water bath, allowed to settle and filtered. On acidifying the filtrate, the coumarinacetic acid came down as an amorphous precipitate which was purified by one or two crystallisations from alcohol or acetic acid. The yield varied in the cases of different phenols and naphthols, that in the case of α -naphthol amounting to 60 per cent. of what is required by theory. The residue insoluble in sodium carbonate was found to consist of the corresponding 4-methyl-coumarin in an almost pure condition, being evidently derived from the partial decomposition of the acetone dicarboxylic acid in the course of the process into aceto-acetic acid and carbon dioxide.

A. DI-COUMARYLS.

I. COMPOUNDS OBTAINED FROM α -NAPHTHAPYRONE-4-ACETIC ACID AND ITS ETHYL ESTER.*3'-Coumaryl-4- α -naphthapyrone.*

Preparation by Perkin's reaction :

Dry sodium- α -naphthapyrone-4-acetate (from 4 grams of the acid), salicylaldehyde (3.3 grams), and acetic anhydride (12 grams) were mixed in a flask and heated on a sand-bath to 150° under reflux for 6 to 7 hours. The product was thrown into water, boiled to decompose the excess of acetic anhydride, and the precipitate digested for a few minutes with sodium carbonate solution. The filtrate gave, on acidification, a small quantity of a brown solid which was found to be too impure and was not investigated further. The dark coloured residue was washed with small amounts of hot glacial acetic acid in order to remove tarry matters and other impurities, dried in the air, and crystallised by dissolving in hot nitrobenzene and diluting with alcohol. Shinning pale yellow needles came down which melted at 255°C (uncorr.), the pure crystals weighing more than 2.5 grams. (Found: $\text{C}=77.30$, $\text{H}=3.69$. $\text{C}_{22}\text{H}_{12}\text{O}_4$ requires $\text{C}=77.64$, $\text{H}=3.53$ per cent.)

Preparation by Knoevenagel's reaction :

Salicylaldehyde (3 grams), α -naphthapyrone-4-ethyl acetate (5.6 grams), and absolute alcohol (50 c.c.) were mixed together and treated with 5 to 6 drops of piperidine, the mixture turning a deep yellow colour. It was heated to boiling on a water-bath under a reflux condenser when the clear yellow solution slowly became turbid and in less than half an hour fine yellow crystals began to separate out. At the end of about two hours the contents of the flask had very nearly solidified, when

the precipitate was filtered off, and the filtrate heated again in the water-bath for another 2 to 3 hours, a further crop of crystals being thus obtained. The crystals, after washing with hot alcohol, were found to be quite pure (m. p. 255°), the total yield being nearly 6 grams, corresponding to 80 per cent. of that theoretically obtainable.

3'-coumaryl-4- α -naphthapyrone crystallises in small needles of a pale yellow colour which are practically insoluble in alcohol, ether, benzene, etc., dissolves sparingly in boiling glacial acetic acid and more readily in nitrobenzene. Cold alkalis have no action on the substance, but on boiling with 25 per cent. caustic soda, it slowly goes into solution from which acids precipitate the unchanged substance. If, however, the alkaline solution be faintly acidified at a low temperature (0° to 5°C), a coumarinic acid gradually settles down. The latter is completely soluble in dilute sodium carbonate, but on allowing to stand at the ordinary temperature for some time or in boiling with water, it quickly loses this property and becomes insoluble in cold alkalis showing that reversion to coumarin had taken place. All attempts to convert the dicoumaryl into the stable coumaric acid either by boiling with concentrated alkali or with bisulphite and alkali were unsuccessful.

6'-Bromo-3'-coumaryl-4- α -naphthapyrone.

This was prepared by boiling an alcoholic solution of α -naphthapyrone-4-ethylacetate (3 grams) and 5-bromosalicylaldehyde (2.5 gram) with a few drops of piperidine in the manner described in the preceding case. Crystallisation from nitrobenzene and acetic acid gave more than 3 grams of yellow needles melting at 292°C (uncorr.) (Found: Br=19.85. $C_{22}H_{11}O_4$.Br requires Br=19.09 per cent.)

6'-Chloro-3'-coumaryl-4- α -naphthapyrone.

This was obtained from 5-chloro-salicylaldehyde and α -naphthapyrone-4-ethylacetate by Knoevenagel's reaction in a yield of nearly 80 per cent. of that required by theory. It crystallised from nitrobenzene and alcohol in pale yellow needles melting at 276°-277°. (Found: Cl=9.54. $C_{22}H_{11}O_4$ Cl requires Cl=9.48 per cent.)

6':8'-Dichloro-3'-coumaryl-4- α -naphthapyrone, prepared from 3:5-dichloro-salicylaldehyde, crystallised in magnificent golden yellow needles, melting at 301°C. (Found Cl=17.34. $C_{22}H_{10}O_4Cl_2$ requires Cl=17.36 per cent.)

6'-Nitro-3'-coumaryl-4- α -naphthapyrone, prepared from 5-nitro-salicylaldehyde, crystallised in deep yellow needles darkening at 310°C and gradually decomposing above this temperature. The substance dissolves readily in warm dilute caustic soda, with a deep red colour from which, on acidifying in the cold, a fairly stable coumarinic acid can be isolated. (Found: C=68.63, H=2.96. $C_{22}H_{11}O_6N$ requires C=68.57, H=2.85 per cent.)

7'-Acetoxy-3'-coumaryl-4- α -naphthapyrone.

Resorcylic aldehyde (2.75 grams), sodium α -naphthapyrone-4-acetate (5.5 grams), and acetic anhydride (10 grams) were heated together for 6 hours at 160°-170°C, and the resulting product poured into excess of water. The dark brown precipitate was washed with hot water, digested for sometime with 10 per cent. caustic soda, and the residual yellowish brown powder crystallised twice from hot nitrobenzene with the addition of alcohol. Deep yellow prismatic needles were deposited darkening at 270° and melting at 282°-284°C. (Found: C=72.81, H=3.75. $C_{24}H_{14}O_6$ requires C=72.36, H=3.52 per cent.)

Attempts to hydrolyse the substance always resulted in the production of a dark pasty mass which could not be purified.

3'- β -Naphthacoumaryl-4- α -naphthapyrone.

2-Hydroxy-1-naphthaldehyde (2 grams) α -naphthapyrone-4-ethylacetate (3 grams) and absolute alcohol (30 c.c.) were boiled with a few drops of piperidine under a reflux condenser for 3-4 hours. The precipitated solid was washed with boiling alcohol and then crystallised from nitrobenzene which gave small fibrous crystals of a pale yellow colour which did not melt or darken even at 310° C. An interesting point to be noted about this compound is its colour which is much lighter in shade than that of most of the other coumaryl- α -naphthapyrones, although its molecular complexity is much greater. (Found: C=79.8, H=3.7. $C_{28}H_{14}O_4$ requires C=80.0, H=3.59 per cent.)

II. DICOUMARYLS FROM β -NAPHTHAPYRONE-4-ETHYL ACETATE.

3'-Coumaryl-4- β -naphthapyrone.

4 grams of the ester, 2 grams of salicylaldehyde, and 6 drops of piperidine were boiled with 50 c.c. alcohol for about 12 hours. The reaction occurred much less readily than in the case of the α -naphthapyrone ethylacetate, and the precipitated solid had to be repeatedly filtered off and the filtrate re-heated before a satisfactory yield could be obtained. Light yellow needles were obtained after one crystallisation from nitrobenzene and alcohol, melting at 282° C (uncorr.). The yield amounted to 1.6 grams. (Found: C=77.18, H=3.46. $C_{22}H_{12}O_4$ requires C=77.64, H=3.53 per cent.)

6'-Chloro-3'-coumaryl-4-β-naphthapyrone, from 5-chloro-salicylaldehyde and β-naphthapyrone ethylacetate, crystallised from a large excess of glacial acetic acid in hard prismatic needles of a very pale yellow colour which darkened at 270°, and melted at 276°—278°. (Found: Cl=8.97. $C_{23}H_{11}O_4Cl$ requires Cl=9.48 per cent.)

6'-Bromo-3'-coumaryl-4-β-naphthapyrone.

This was prepared in the usual way from 5-bromo-salicylaldehyde (4 grams), and the pyrone ester (6 grams), by boiling in alcoholic solution in the presence of piperidine for several hours. It was deposited from acetic acid in short yellow prismatic needles melting at 260°. (Found: Br=19.21. $C_{22}H_{11}O_4Br$ requires Br=19.09 per cent.)

III. DICOUMARYLS FROM 7-METHYL-COUMARIN-4-ACETIC ESTER.

7-Methyl-4:3'-dicoumaryl.

This was prepared both by Perkin's reaction from salicylaldehyde, sodium-7-methyl-coumarin-4-acetate and acetic anhydride, and by Knoevenagel's reaction from the ester (5 grams) and aldehyde (3 grams) and a little piperidine. The latter process gave the better yield amounting to a little over 70 per cent. of that obtainable by theory. It crystallised from acetic acid in soft colourless wooly needles melting at 247° C. (Found: C=75.14, H=4.12. $C_{19}H_{12}O_4$ requires C=75.00, H=3.95 per cent.)

7-Methyl-6'-bromo-4:3'-dicoumaryl.

It was prepared by the condensation of 5-bromo-salicylaldehyde (4 grams) with 7-methyl-coumarin ethyl

acetate (5 grams) in the presence of piperidine in the usual way. Crystallisation from nitrobenzene diluted with acetic acid yielded colourless ferny needles melting at 292° . (Found: Br = 20.59. $C_{19}H_{11}O_4Br$ requires Br = 20.88 per cent.)

7-Methyl-6'-chloro-4:3'-dicoumaryl, from the corresponding chloro-salicylaldehyde, crystallised from acetic acid in colourless silky needles melting at $288^{\circ}C$. (Found: Cl = 10.23. $C_{19}H_{11}O_4Cl$ requires Cl = 10.49 per cent.)

7-Methyl-6':8'-dichloro-4:3'-dicoumaryl, prepared from 3:5-dichloro-salicylaldehyde, crystallised in pale yellow needles melting at $286^{\circ}C$. (Found: Cl = 19.41. $C_{19}H_{10}O_4Cl_2$ requires Cl = 19.04 per cent.)

Action of Alkalis on 7-Methyl-4:3'-dicoumaryl.

The substance dissolves with great difficulty in alkalis, more than two hours, boiling with excess of 10 per cent. caustic soda being found necessary to get it into solution. A neutral solution to litmus or phenolphthalein of the sodium salt of the coumarinic acid could not be prepared by the usual methods, the sodium coumarinate in aqueous solutions being alkaline to test papers. Dilute nitric acid was, therefore, cautiously added in the cold till there was just a trace of a permanent precipitate. This was filtered off and the pale yellow silver salt was precipitated from the filtrate by adding a slight excess of silver nitrate. The salt after drying on a porous plate in the vacuum, was analysed. (Found: Ag = 41.48. $C_{19}H_{12}O_5Ag_2$ requires Ag = 40.37 per cent.)

The analysis seems to show that the acid is formed by the opening up of only *one* of the pyrone rings, this being presumably derived from the coumarin ring in which the 3 position is free, as substitution in the latter position has been observed to have a great hindering effect on the opening of the pyrone nucleus.

3: (?) -Dibromo-7-methyl-4:3'-dicoumaryl.

The dicoumaryl (3 gms.), bromine (2 c.c.) and glacial acetic acid (25 c.c.) were boiled together under a reflux condenser with the addition of a trace of iodine, until the colour of the bromine vapour had practically disappeared. The dibromo-derivative which was almost insoluble in acetic acid was collected, washed with hot acetic acid, and crystallised twice from nitrobenzene. It formed colourless hexagonal plates melting at $280^{\circ}\text{--}32^{\circ}\text{C}$. (Found: $\text{Br}=34.92$. $\text{C}_{18}\text{H}_{10}\text{O}_4\text{Br}_2$ requires $\text{Br}=34.63$ per cent.)

6'-Methyl-(?)-bromo-3-(3'-coumaryl)-benzofuran-2-carboxylic Acid.

The above dibromo-compound (1.5 gms.) was finely powdered and boiled for about an hour with a 40 per cent. solution of caustic soda (6 grams) and alcohol (10 c.c.), when the sodium salt of the above acid separated out as a shining crystalline mass. This was collected, dissolved in water and the solution acidified when a bulky white gelatinous precipitate came down, which became granular and easy to filter on boiling. It was completely soluble in cold sodium carbonate, and dissolved in strong sulphuric acid with a yellow colour which, on warming, turned deep red in the manner of the coumarones. Crystallisation from glacial acetic acid gave colourless thin needles melting at 260°C with evolution of gas. (Found: $\text{Br}=19.67$. $\text{C}_{18}\text{H}_{11}\text{O}_5\text{Br}$ requires $\text{Br}=20.05$ per cent.)

IV. DICOUMARYLS FROM 7-HYDROXY-COUMARIN-4-ACETIC ACID.

7-Hydroxy-4:3'-dicoumaryl.

This was obtained in an excellent yield by the condensation of 7-hydroxy-coumarin ethyl-acetate and

salicylaldehyde in the presence of piperidine. It crystallised from dilute acetic acid in small colourless needles darkening at 300° , and melting at 311°C . A noteworthy feature of this compound is its property of dissolving in dilute alkalis with a yellow colour without the least fluorescence, although both 7-hydroxy-4-methyl-coumarin and 7-hydroxy-coumarin-4-acetic acid are strongly fluorescent in alkaline solutions. (Found: $\text{C}=71.01$, $\text{H}=3.45$. $\text{C}_{18}\text{H}_{10}\text{O}_5$ requires $\text{C}=70.58$, $\text{H}=3.27$ per cent.)

Its *acetyl* derivative, prepared by the action on it of acetic anhydride and fused sodium acetate, crystallises from acetic acid in colourless woolly needles and melts at 253°C .

Its *benzoyl* derivative formed by benzoylating in pyridine solution was obtained in colourless needles melting at 234°C .

7-Methoxy-4:3'-dicoumaryl was prepared synthetically from the 7-methoxy-coumarin ethylacetate. It formed small prismatic needles melting at 241°C . (Found: $\text{C}=71.00$, $\text{H}=3.41$. $\text{C}_{19}\text{H}_{12}\text{O}_6$ requires $\text{C}=71.25$, $\text{H}=3.75$ per cent.)

7-Hydroxy-6'-bromo-4:3'-dicoumaryl.

This was obtained in a good yield from 5-bromo-salicylaldehyde and 7-hydroxy-coumarin ethylacetate by Knoevenagel's reaction. It crystallised from glacial acetic acid in short colourless needles, melting at 308° - 310°C with decomposition. (Found: $\text{Br}=20.56$. $\text{C}_{18}\text{H}_9\text{O}_6\text{Br}$ requires $\text{Br}=20.78$ per cent.)

7-Acetoxy-6'-bromo-4:3'-dicoumaryl crystallises in the form of long woolly needles melting at 247° - 48°C . (Found: $\text{Br}=19.04$. $\text{C}_{20}\text{H}_{11}\text{O}_6\text{Br}$ requires $\text{Br}=18.73$ per cent.)

B. 3-PHENYL-COUMARINS.

6-Chloro-3-phenyl-coumarin.

Dry sodium phenyl acetate (3 grams) 5-chloro-salicylaldehyde (3.5 grams) and acetic anhydride (10 c.c.) were heated to 150° - 60° for 5 hours on the sand-bath, the mixture poured into cold water, and the product worked up in the usual manner. The residue insoluble in sodium carbonate crystallised from 50 per cent. acetic acid in colourless sharp needles melting at 200°C . The sodium carbonate extract on acidification, deposited a small amount of a white precipitate which was an acid, and after crystallisation from alcohol, melted at 190°C . It was presumably the acetoxy-phenyl-coumaric acid, but was not investigated further. (Found: $\text{Cl}=13.82$. $\text{C}_{15}\text{H}_9\text{O}_3\text{Cl}$ requires $\text{Cl}=13.84$ per cent.)

An extraordinarily poor yield of the above compound was obtained by the condensation of the chloro-salicylaldehyde and phenyl-acetic ethyl ester in the presence of piperidine, even after boiling for 8 hours.

6-Bromo-3-phenyl-coumarin was prepared in the same way by Perkin's reaction from 5-bromo-salicylaldehyde and sodium phenylacetate. It formed beautiful silky needles melting at 193°C . (Found: $\text{Br}=26.34$. $\text{C}_{15}\text{H}_9\text{O}_3\text{Br}$ requires $\text{Br}=26.58$ per cent.) Only a trace of this product was obtained by carrying out the condensation by Knoevenagel's process.

6:8-dichloro-3-phenyl-coumarin, from 3:5-dichloro-salicylaldehyde and sodium phenylacetate, crystallised from acetic acid in short glistening prisms melting at 195.5°C . (Found: $\text{Cl}=23.99$. $\text{C}_{15}\text{H}_7\text{O}_3\text{Cl}_2$ requires $\text{Cl}=24.40$ per cent.)

7-Acetoxy-3-phenyl-coumarin was prepared by heating resorcylic aldehyde (4 grams), sodium phenylacetate

(5 grams) and acetic anhydride (12 grams) in an oil bath to 160° - 70° for several hours. It formed colourless crystals insoluble in cold alkalis and melted at 186°C . (Found: $\text{C}=72.66$, $\text{H}=4.10$. $\text{C}_{17}\text{H}_{12}\text{O}_4$ requires $\text{C}=72.85$, $\text{H}=4.28$ per cent.)

7-Hydroxy-3-phenyl-coumarin was prepared by hydrolysing the acetyl derivative with 20 per cent. caustic potash. Crystallisation from alcohol gave fine clusters of tetragonal prisms melting at 209° - 10°C . The alcoholic solution of the substance shows a magnificent purple fluorescence, whilst the alkaline solution exhibits a fine blue fluorescence as in the case of the umbelliferous. (Found: $\text{C}=75.32$, $\text{H}=4.05$. $\text{C}_{15}\text{H}_{10}\text{O}_3$ requires $\text{C}=75.63$ $\text{H}=4.20$ per cent.)

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On the Specific Heat of Liquids

BY

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Prof. Honda¹ proposed a formula for the specific heat of liquids on the basis of rotational energy of the molecule, but Prof. Lindemann² showed that the rotational energy cannot account for the large specific heat of liquids. The author in the present note, proposes an empirical formula for the energy of the liquid per unit mass.

$$E = 3NkT + \frac{N}{2} \frac{x}{(e^x - 1)} \quad \dots \quad (1)$$

where $x = \frac{h\nu_1}{kT}$, and N the number of atoms per unit mass. and ν is given by Lindemann's well known formula³

$$\gamma_1 = 2.08 \times 10^{11} \left[\frac{T_1}{mV^{\frac{2}{3}}} \right]^{\frac{1}{2}} \quad \dots \quad (2)$$

T is the absolute temperature, h and k are Planck's and Boltzman's constants.

From (1) C_v is found to be

$$C_v = 3Nk + \frac{Nk}{2} \frac{e^x x^2}{(e^x - 1)^2} \quad \dots \quad (3)$$

Table (1) gives a few values calculated from (3) and for comparison C_p is given in the last column [Landolt and Bornstein tables].

TABLE I.

Liq.	Abs. Temp.	$\gamma \times 10^{12}$	C_p Cal.	C_v
Cl	200	2.24	.20	.22
Br	270	1.70	.08	.107
Hg	240	1.25	.032	.033
Sn	510	2.24	.059	.064
Bi	610	1.6	.037	.036
Pb	610	1.8	.032	.040
Al	970	7.5	.27	.39
Cs	299	.95	.053	.058
K	335	2.3	.18	.22
Cu	1357	6.7	.12	.15
Li	460	1.0	1.0	1.3
Na	396	3.96	.31	.33
Ag	1300	4.36	.065	.074
Zn	700	4.36	.11	.12

The calculated values are in general less than the experimental values of C_p . Since $C_p - C_v = T\alpha^2/\rho k$ where α is the volume expansion, k the compressibility, and ρ the density, C_v could be computed from the experimental values C_p , but no data seem to be available for compressibility. k for liquids is of the order of 10^{-12} per dyne, hence $C_p - C_v$ is not greater 10^{-2} . Therefore it is believed that the calculated values are fairly close to the true value.

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¹ Phil. Mag., January, 1923

² Phil. Mag., June, 1923.

³ Phys. Zeits., 1910, p. 689.

The Action of Acids and Water upon Magnesium Boride.

BY

RAMES CHANDRA RAY.

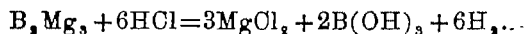
In his systematic researches on the action of magnesium on oxygen compounds, Winckler (Ber., 1890, 23, 722) studied the reaction between magnesium and boron trioxide, and from the results of analyses of the products of the reaction, he drew the conclusion that two borides were formed, one having the formula Mg_3B_2 and the other Mg_2B_3 . Moissan [Compt. rend., 1892, 114, 392; also Ann. Chim. Phys., 1895 (VII), 6, 296] has also mentioned of two borides of magnesium one of which was unstable and decomposable by water and the other did not react either with water or with hydrochloric or nitric acid. The latter substance was obtained in a crystalline form. The crystalline substance, which Moissan supposed to be another magnesium boride, appears to be crystalline boron, a certain amount of which is always formed in the preparation of magnesium boride, depending upon the temperature and duration of heating. It has been shown in a previous communication (Jour. Chem. Soc., 1914, 105, 2162) that at a red heat and under normal pressure only one boride having the formula, Mg_3B_2 , is formed, and on heating the boride, magnesium is driven off and the greater part of the boron separates in the crystalline state. On heating the so-called amorphous boron with magnesium the same boride, with a small quantity of magnesium oxide, is obtained.

The product obtained by heating a mixture of 1 part of boron trioxide and 2·2 parts of magnesium powder to a

red-heat in a current of hydrogen for 45 minutes was almost completely soluble in dilute hydrochloric acid, and appeared, from the results of analyses, to consist of magnesium boride, Mg_3B_2 , and magnesium oxide in the theoretical proportions. One of the samples of crude boride, prepared in the abovementioned manner, was found to consist of:—

Magnesium	64.71 per cent.
Boron as boride (soluble in dilute HCl)	...	8.72	„ „
Residue insoluble in dilute HCl (free boron, etc.)	...	2.46	„ „
Oxygen (by difference)	...	24.11	„ „

and one gram yielded, when dissolved in acid, 0.0472 gram of hydrogen, whilst one gram of a substance containing 8.72 per cent. of boron as the boride Mg_3B_2 should yield 0.0476 gram of hydrogen according to the equation:—



Jones (Trans. Chem. Soc., 1879, 35, 41) and two years later, Jones and Taylor (*ibid.*, 1881, 39, 213) studied the action of hydrochloric acid on magnesium boride. They obtained a gaseous boron hydride to which they assigned the formula BH_3 but they could not isolate it from the large quantity of hydrogen which was evolved at the same time. Their work was confirmed in a qualitative manner by Sabatier (Compt. rend., 1891, 112, 866). Ramsay and Hatfield (Proc. Chem. Soc., 1901, 17, 152) found that on passing the gas evolved by the action of dilute acids on magnesium boride through a bulb cooled in liquid air, a solid substance was deposited which, when the bulb was warmed, volatilised and could be collected as a gas. From the results of analyses of the gas, and its density, its formula appeared to be B_2H_6 ; but it appeared to consist of two isomeric substances, one stable and the other unstable and readily decomposed by

reagents. Ramsay and Hatfield, however, were subsequently unable to duplicate the work.

Stock and his co-workers (Stock and Massenez, Ber., 1912, 45, 3539; Stock and Friederici, *ibid*, 1913, 46, 1959; Stock, Friederici and Priess, *ibid*, 1913, 46, 3353; Stock, Zeits. Electrochem, 1913, 19, 779; Stock, Kuss and Priess, Ber., 1914, 47, 3115; Stock and Kuss, Ber., 1923, 56 [B] 789) succeeded in isolating several boron hydrides by dropping finely powdered magnesium boride into 15 per cent. hydrochloric acid at 50° to 80°. According to them at least ten boron hydrides exist, of which they have obtained the following in a pure condition:—

(a) B_2H_6 (B.p.-91°), (b) B_4H_{10} (B.p.-18°), (c) B_5H_9 (liquid; Vap. Press. at 0° 64 mm.), (d) B_6H_{10} (liquid Vap. Press. at 0° 7 mm.), (e) $B_{10}H_{14}$ (crystalline solid; M.p. 99°).

In spite of careful examination they have failed to find the slightest indication of a boron hydride containing one atom of boron in the molecule. They have also shown that all the boron hydrides react with water with the formation of boric acid and liberation of hydrogen.

It has already been shown that when magnesium boride is treated with dilute acids, and the gases evolved kept in contact with the acid for a short time, the residual gas contains only hydrogen. Boric acid and the magnesium salt of the acid employed in the reaction are found in the solution, and for every molecule of magnesium boride, Mg_3B_2 , six molecules of hydrogen are evolved. It appears probable that the boron hydride or hydrides which are first formed by the action of the acid on magnesium boride, are completely decomposed by the action of water. The failure of the earlier workers in preparing boron hydrides is perhaps mainly attributable to this cause.

The action of water on magnesium boride, on the other hand, appears to be entirely different. When

water is added to magnesium boride, which always contains a certain amount of magnesium oxide, the reaction takes place with evolution of a considerable quantity of heat, and hydrogen is liberated, containing only traces of boron hydrides, which impart to it a characteristic unpleasant odour, but no boric acid or magnesium borate is formed in the reaction. The amount of hydrogen given off by the action of water is only one-half of that liberated by the action of dilute acid. The solution contains only a small quantity of boron as borohydrates, the properties of which have been described by Travers, Ray and Gupta (Pamphlet, H. K. Lewis & Co., London, 1916).

A sample of magnesium boride was prepared by heating amorphous boron (a chocolate brown powder) with magnesium powder in a magnesia-lined crucible, a rapid current of hydrogen being passed into it from the commencement of the experiment until the crucible was cold. The magnesium boride gave, on analyses, the following results:—

Insoluble (crystalline boron, etc.)	...	0.76	per cent.
Magnesium	...	74.13	" "
Boron (soluble in acid)	...	18.76	" "
Oxygen (by difference)	...	6.35	" "
Magnesium as oxide	...	9.51	" "
Magnesium as boride	...	64.62	" "
Boron as boride	...	18.76	" "

It was treated with water and the hydrogen evolved was collected and measured. A weighed quantity of the substance was introduced into a flask and a measured volume of water was added to it. The mouth of the flask was quickly closed with a rubber stopper provided with a delivery tube, dipping under water. The volume of hydrogen evolved was measured from time to time. When the rate of evolution of hydrogen fell to less than 3 c.c. per gram of boride in twenty-four hours the

experiment was brought to an end. The following results were obtained:—

Time in hours	...	20	40	60	90	114	138	186	258	306	426
Volume of hydrogen in c.c. at N. T. P. per gram of boride	...	144	204	286	345	402	440	480	512	528	543

During the experiment the water in contact with the boride was changed several times and the amount of boron in each of the solutions was estimated. The total quantity of boron removed as soluble borohydrate in the course of the experiment was approximately 0.02 gram per gram of boride. One gram of the boride contained 0.1876 gram of boron as boride, so that only 10 per cent. of the boron in the magnesium boride went into solution as borohydrates.

The results are plotted in Fig. 1. It will be observed

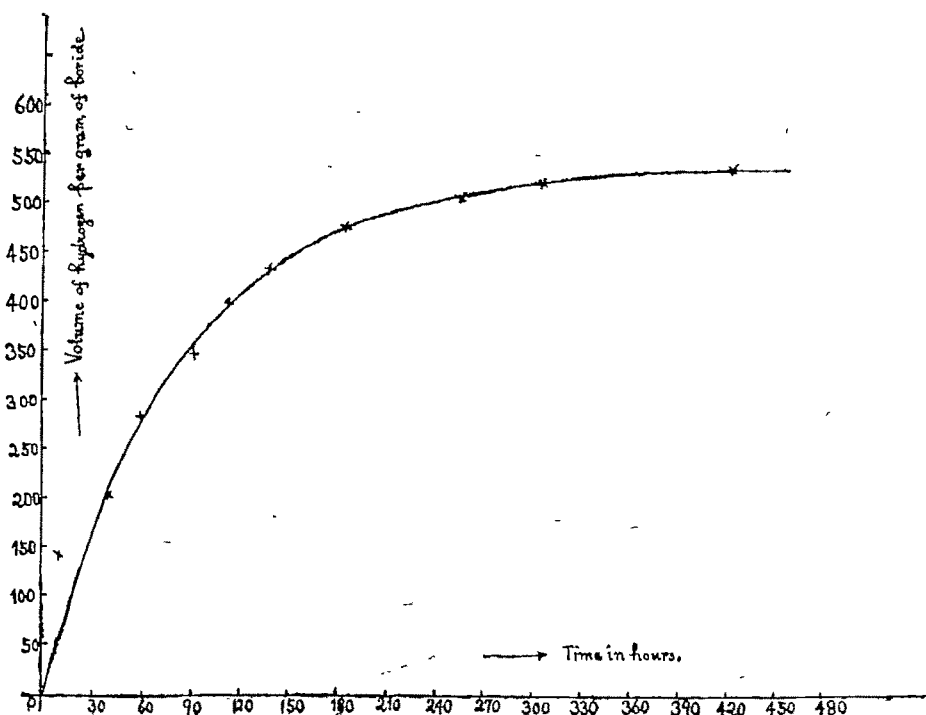
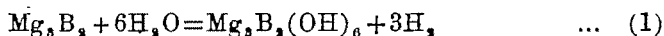
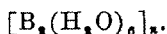


Fig. 1.

that the rate of evolution of hydrogen is very rapid at first, gradually falls off, and finally reaches a limiting value. The total quantity of hydrogen evolved after 426 hours is 543 c.c. or 0.0489 gram per gram of boride and this amount very nearly approaches the limiting value of the quantity of hydrogen which would be evolved on treating the boride with water for a very long time, that is, until the reaction is complete. One gram of the boride when treated with dilute hydrochloric acid gave off 0.1040 gram of hydrogen, and one-half of this quantity, 0.0520 gram is very nearly equal to the amount of hydrogen liberated by the action of water. The slightly lower value actually obtained is probably due to the fact that the reaction between water and the boride was not quite complete. The reaction of water on magnesium boride has been studied more fully in collaboration with Travers and Gupta (*loc. cit.*). From the amount of hydrogen evolved per gram of magnesium boride and analyses of the residue from action of water on the boride, it has been shown that the reaction takes place according to the equation:—

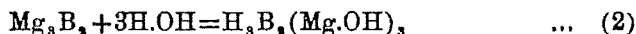


That this is mainly the reaction, which takes place between water and magnesium boride, has been proved by the action of dilute hydrochloric acid and ammonia on the "spent boride." The product of the reaction with water appears to be completely insoluble in and inactive towards both hot and cold water and may be regarded as the magnesium salt of a borohydrate of the formula

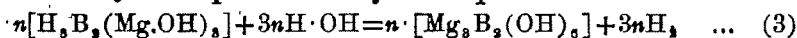


It is not improbable that, as shown by Schwarz and Konrad (Ber., 1922, 55, [B], 3242) in the case of the action of water on magnesium silicide, Mg_2Si , the first product of decomposition is a compound of the formula

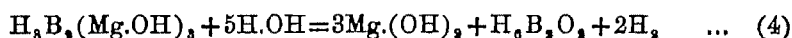
$\text{H}_3\text{B}_2(\text{Mg.OH})_3$, and the reaction may be expressed by the equation:—



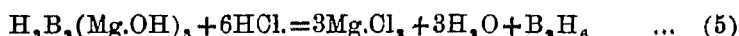
This primary product then suffers further hydrolysis which may be represented by the equation:



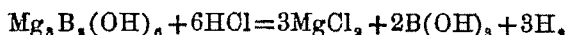
About 90 per cent. of the initial product undergoes decomposition according to equation (3) which is the main reaction between water and magnesium boride. The formation of borohydrates and hydroborons, which are undoubtedly produced by secondary reactions, probably takes place according to the following scheme:—



and



Only about 10 per cent. of the magnesium boride or the primary product of the action of water upon it undergoes decomposition according to the equation (4) or (5), and this accounts for the small yield of borohydrates or hydroborons obtained in the reactions with water or acids. Contrary to what has been generally supposed no boric acid or magnesium borate is formed in the reaction with water. The formation of boric acid takes place by the decomposition of the compound $\text{Mg}_3\text{B}_2(\text{OH})_6$ according to the equation:—



or by the decomposition of the hydrides of boron, all of which, as has been shown by Stock and his collaborators (*loc. cit.*), react readily with water with evolution of hydrogen and formation of boric acid.

Summary.

(1) When magnesium boride is treated with water the quantity of hydrogen liberated is only one-half of

that obtained by the action of dilute acids upon it. In the reaction between water and magnesium boride, no boric acid or magnesium borate is formed.

(2) The mechanism of the action of water and dilute acids upon magnesium boride, and of the formation of borohydrates and hydrides of boron, has been suggested.

The author's best thanks are due to Prof. F. G. Donnan, F.R.S., and to Dr. M. W. Travers, F.R.S., for their kind interest and helpful criticisms.

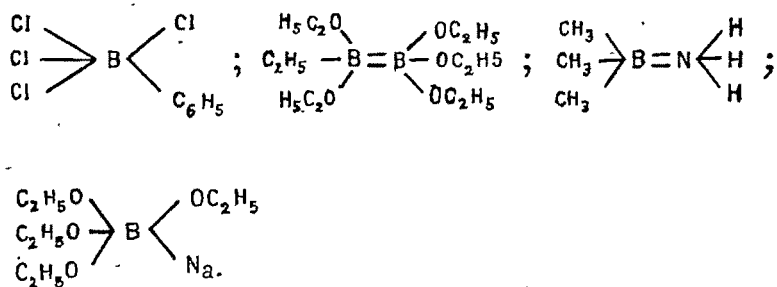
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The Valency of Boron.

BY

RAMES CHANDRA RAY.

From the chemical point of view, boron is decidedly a non-metallic element. It is trivalent in its halogen derivatives and the trivalent nature is also exhibited in most of its compounds. However, under certain conditions it appears to possess a valency of five. Moissan (*Compt. rend.*, 1892, *115*, 271) has prepared boron penta-sulphide. A few other compounds of boron, containing organic radicles, such as $\text{C}_6\text{H}_5\cdot\text{B}\cdot\text{Cl}_2$, $(\text{CH}_3)_3\text{B}:\text{NH}_3$, $\text{C}_2\text{H}_5(\text{C}_2\text{H}_5\text{O})_2\text{B}:\text{B}(\text{OC}_2\text{H}_5)_3$, $(\text{C}_2\text{H}_5\text{O})_3\text{B}\cdot\text{OC}_2\text{H}_5\cdot\text{Na}$, etc., described by Michaelis and Becker (*Ber.* 1880, *13*, 58); Frankland and Duppa (*Phil. Trans.*, 1862, *152*, 167; *Proc. Roy. Soc.*, 1876, *25*, 165), and Copaux (*Compt. rend.*, 1898, *127*, 719) probably contains pentavalent boron and may be formulated thus:—



The compound $(\text{CH}_3)_3\text{B}:\text{NH}_3$ is fairly stable; it melts at 51° and boils at 110° . The existence of certain additive compounds of boron trihaloids also suggests the pentavalent nature of the element.

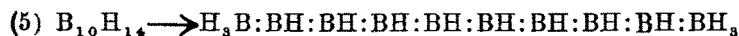
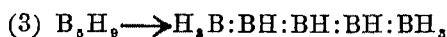
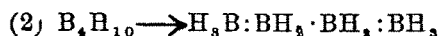
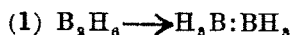
Stock and his co-workers (Stock and Massenez, Ber., 1912, 45, 3539; Stock and Frederici, *ibid*, 1913, 46, 1959; Stock, Frederici and Priess, *ibid*, 1913, 46, 3353; Stock, Z. Electrochem., 1913, 19, 779; Stock, Kuss and Priess, Ber., 1914, 47, 3115) have suggested that boron is quadrivalent in the case of its hydrides and certain compounds derived from it, but except in cases in which the composition of the substance is doubtful or the molecular formulæ has not been determined, it is possible to assign formulæ to all these compounds on the assumption that boron is always trivalent or pentavalent. Further, as has been pointed out by Huggins (J. Phys. Chem., 1922, 26, 833) "that in the light of the present-day evidence in regard to atomic structure, it does not seem likely that boron can be quadrivalent in the sense that carbon is quadrivalent—that in these substances each boron atom can directly be bonded, through electron pairs, to four other atoms." Huggins suggests that boron is trivalent in all the hydrides, and the hydrogen atoms are held by means of four electron bonds and each such four electron bond is surrounded by four atoms. For the four hydrides, B_2H_6 , B_4H_{10} , B_6H_{12} , and $B_{10}H_{14}$, Huggins assigns structures similar to those adopted by him (Jour. Am. Chem. Soc., 1922, 44, 1607; Science, 1922, 55, 678) for ethylene ($H_2C=CH_2$), butadiene ($H_2C=CH-CH=CH_2$), benzene (C_6H_6) and naphthalene ($C_{10}H_8$), respectively. But these unusual structures must be very unstable and although they may be strong enough for holding together the hydrogen atoms, they are extremely unsuitable for molecules having larger atomic kernels. They are incapable of explaining the structure of the borohydrates, which undoubtedly possess very similar constitution as the hydrides, as well as the halogen derivatives such as, B_2H_5Cl and $B_2H_4O_2$. It has been pointed out in a previous paper (Jour. Chem. Soc., 1922,

121, 1088) that the group,

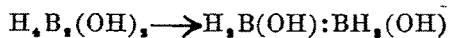


appears to be a fairly stable one and is present in the hydrides, the borohydrates, the halogen derivatives of the hydrides, and Frankland's compound $\text{C}_2\text{H}_5\text{B}(\text{OC}_2\text{H}_5)_2$: $\text{B}(\text{OC}_2\text{H}_5)_3$.

The five hydrides of boron isolated by Stock and his collaborators (*l. c.*) may be assigned the following formulæ:—

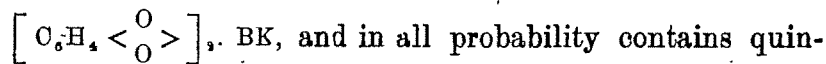


To the borohydrate $\text{H}_4\text{B}_2(\text{OH})_2$, and the halogen derivatives, $\text{B}_2\text{H}_5\text{X}$ and $\text{B}_2\text{H}_4\text{X}_2$, all of which correspond to the hydride B_2H_6 , may be given the formulæ:—



The difficulty about the structure of the hydrides and the corresponding compounds disappears if the more natural assumption, that boron exhibits a negative valency of five in these compounds, be adopted. Frankland (*loc. cit.*) was the first to suggest the possibility of a quinquevalent boron atom corresponding to that

of nitrogen, phosphorus and arsenic. More recently, Hermans (Proc. K. Acad. Wetench. Amsterdam, 1923, 26, 32) has prepared the crystalline potassium salt of pyrocatecholboric acid, and its composition has been found to be $C_{12}H_8O_4BK$. The only plausible structure is



quevalent boron. In a paper on the valency of boron Böeseken (*ibid*, 1923, 26, 97) has discussed the possibility of the boron atom functioning as a quinquevalent and quadrivalent element according to the Lewis-Langmuir theory of valency. He has shown that the oldest known type of compound in which boron is to be regarded as quinquevalent is the type $HB F_4$. In boron fluoride, BF_3 , the outer electron ring of the boron atom contains six electrons shared in pairs with the fluorine atoms. When combining with another molecule of hydrogen fluoride, the boron atom completes its octet by sharing with the new fluorine atom one of the electrons of the latter and a hydrogen electron. By taking the hydrogen electron, however, it forms the negative ion BF_4^- and the positive ion H^+ .

Of the modern theories of the structure of atoms, although the Lewis-Langmuir theory of fixed electrons appears better suited to explain chemical facts, the balance of evidence is in favour of Bohr's revolving electron quantum theory. According to the latter, the boron atom consists of the helium structure of two electrons revolving in uni-quantum orbits and in addition 3 electrons in 2-quantum orbits of type 2. These three electrons can each share the outer ring of three halogen atoms thus completing their octets or five additional electrons can gather round the boron atom and complete its own octet. This corresponds to Abegg and Bodlander's theory of Valency (Z. Anorg. Chem., 1899, 20, 453; *ibid*, 1904,

39, 330) which states that the sum of the maximum negative and positive valencies of an element equals eight. In the present considerations of the structure of the boron hydrides and borohydrates the compounds will be expressed in terms of the fixed electron atom, as this type of atom is more suitable for graphical representation. So far as the structures of the compounds are concerned they would remain almost the same whichever type of atom be assumed.

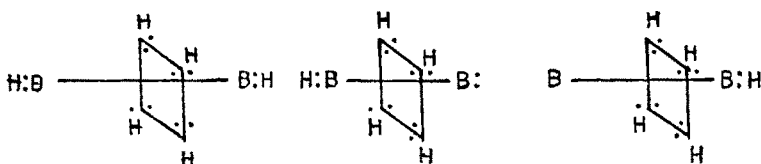
An important factor in determining the valency of an element is the place of the element in the atomic number scale relative to the place of the nearest non-valent gases. There are, thus, two valency-determining distances for each element, the one, the distance below a non-valent gas, determines the negative valency and the other, the distance above a non-valent gas, determines the positive valency of the element. Boron is three places above helium and five places below neon so that it is expected to possess a positive valency of three and a negative valency of five. The negative valency if it is exhibited at all, will be much weaker than the positive valency. If boron really exhibited a negative valency of five the question naturally arises, "Why does not a compound of the formula BH_5 exist?" It is easy to picture BH_5 as a neon system of electrons, completed by the single electrons of five hydrogen atoms with the five hydrogen nuclei arranged externally. By calculating the "mean collision areas" from the results of measurements of the viscosity of various gaseous hydrides, Rankine (Trans. Faraday Soc., 1922, 17, 719) has shown that as the number of hydrogen atoms in the molecule increases their nuclei become more and more remote from the nucleus of the central atom. He has suggested "that it is reasonable to suppose that this retreat of the hydrogen nuclei is due to the fact that they exert mutual

repulsion on one another, and that would naturally tend to drive them further apart with each addition. The effect finally leads to the failure to form such molecules as BH_5 , which may be theoretically possible but are unstable owing to the repulsion of the numerous hydrogen nuclei."

If this view is accepted, it is easy to understand the simultaneous formation of several hydrides of boron by the action of acids on magnesium boride. The molecules of BH_3 , which may be supposed to be temporarily formed, break up on account of the mutual repulsion of the hydrogen nuclei, and from this results the formation of several more complex molecules containing more than one atom of boron. The hydride B_2H_6 , for example, is formed by the linking of two BH_3 -groups and B_4H_{10} from two BH_3 -groups and two BH_2 -groups.

It has been shown by J. J. Thomson (Phil. Mag. 1921 [vi], 41, 520) that the attachment of a 1 one-electron atom like that of hydrogen requires two electrons on the layer round the atom with which it is combined. Lewis (Trans. Faraday. Soc., 1923, 19, 452) has emphasised the fact that the formation of the electron pair is the most important phenomenon in all chemical combinations. Although the quantum theory at present gives no adequate explanation of the pairing of electrons to form a single bond, and although it is difficult to reconcile it with the undoubted existence and apparent stability of H_2 (J. J. Thomson, *ibid*, 1923, 19, 476) where one electron holds two nuclei together, the universality of this pairing of electrons in the binding of atoms appears to point definitely to an actual physical coupling of electronic orbits. As it is not possible for five hydrogen atoms to become attached to a single atom of boron, no hydride containing a single atom of boron is formed. The structure of the two gaseous hydrides, B_2H_6 and B_4H_{10}

may be illustrated thus:—



The two end hydrogen atoms, in the first compound are replaceable by hydroxyls or halogens and give rise to the compounds $B_2H_4(OH)_2$ and $B_2H_4X_2$. The suggested structure resembles the crystalline form of the potassium salt, $B_2H_4(OK)_2$ which crystallises as octahedrons. Little is known of the properties of the hydrides of boron and further experimental evidence is necessary before these or any other proposed structures may be considered as correct. For the investigation of the connection between atomic structure and chemical properties, however, the study of the boron atom in the formation of the hydrides and the related compounds is of great interest.

Summary.

(1) The valency of boron is discussed. Although in most of its compounds, the elements exhibit a positive valency of 3, under certain circumstances, especially in the case of the hydrides and certain related compounds, it appears to possess a negative valency of 5.

(2) Structures are proposed for the hydroborons, borohydrates, and the halogen derivatives of the boron hydrides.

In conclusion I wish to express my thanks to Prof. F. G. Donnan, F.R.S., and Dr. M. W. Travers, F.R.S., for their kind interest.

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[Received July 7, 1934]

Hetero-ring Formations with Thiocarbohydrazide.

BY

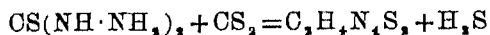
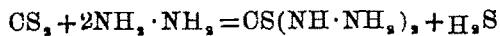
PRAPHULLACHANDRA GUHA

AND

SATISHCHANDRA DE.

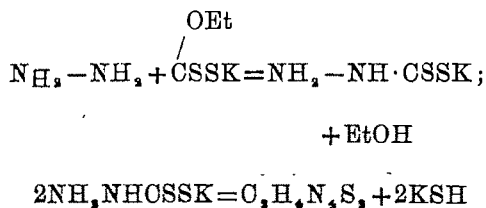
In a previous paper, it has been shown that dithio-*p*-urazine can be prepared from thiocarbohydrazide by the action of potassium ethyl xanthate and it has also been suggested there that the compound $C_2H_4N_4S_2$ of Purgotti and Vigano, (Gazzetta, 1901, 31, ii, 563) which they regarded as dithio-*p*-urazine was probably a thiodiazole compound (Trans., 1924, 125, 1215). Arndt and Bieliich (Ber., 1923, 56, 809) by repeating the experiment of Purgotti and Vigano, could not get the so-called dithio-*p*-urazine of Purgotti, and obtained a compound of the same composition but differing in properties and ascribed to the new compound the formula of N-4-amino-dithio-urazole.

Two more improved methods have now been discovered for the preparation of dithio-*p*-urazine. For the desired synthesis, the use of thiocarbohydrazide has been dispensed with and it has been achieved by allowing hydrazine hydrate to react directly with carbondisulphide. The mechanism of the reaction is as follows :



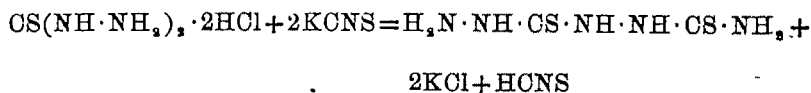
That the above scheme of reaction is correct, has been proved by synthesising dithio-*p*-urazine from thiocarbohydrazide and carbondisulphide.

Potassium ethyl xanthate yields dithio-*p*-urazine by reacting with hydrazine hydrate much more easily (*vide* expt.). Potassium-dithiocarbazinate formed by the action of hydrazine and potassium ethyl xanthate, reacting with another molecule of the same substance and with the elimination of two molecules of potassium hydrosulphide produces one molecule of dithio-*p*-urazine, thus :



Dithio-*p*-urazine has been desulphurised by treatment with mercuric oxide yielding *p*-urazine. The above reaction lends additional support to the dithio-*p*-urazine structure for our compound.

One molecule of potassium sulphocyanide reacts with one molecule of thiocarbonylhydrazide yielding mainly thiocarbonylhydrazido-thiocarbonamide.

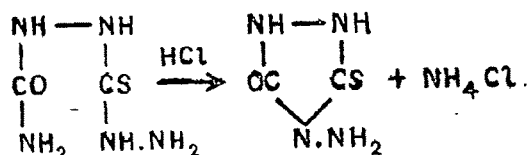


Besides this, there is also formed a very small quantity of a light yellow-coloured substance which could not be further studied for want of sufficient quantity of this material.

The closure of the ring of the above thiocarbonylhydrazido-thiocarbonamide has been effected with the aid of strong hydrochloric acid, when the thio-compound loses one molecule of ammonia with the formation of the hydrochloride of N-4-aminodithiourazole of Arndt and Bielich, from which the free base can be easily liberated by sodium acetate. The identity of this compound with that of

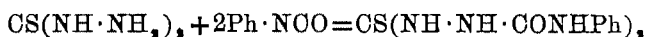
Arndt and Bielich has been established by preparing the benzal derivative, the dibenzylthio-ether and the disulphide; all of them melting at the same temperature as the corresponding derivatives of Arndt and Bielich compound.

The behaviour of potassium cyanate towards thiocarbohydrazide has also been studied and it has been found that the reaction proceeds exactly in a similar fashion as in the case of potassium sulphocyanide; the resulting thiocarbohydrazido-carbonamide, $\text{NH}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{CONH}_2$ in its turn, gives N-4-amino-monothiourazole:



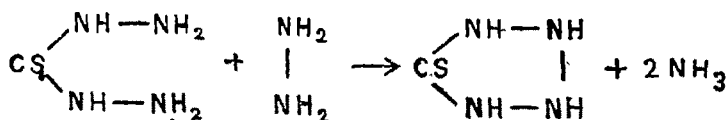
(Compare Freund and Imgart, Ber., 28, 946.) The presence of one mercaptanic group and the hydrazine residue in the compound is proved by the fact that it gives a disulphide with iodine and a monobenzal-derivative with benzaldehyde.

Phenyl isocyanate differs in its behaviour towards thio-carbohydrazide from potassium cyanate and thiocyanate in the sense that both of the hadrazino groups are attacked by the reagent yielding *s*-di-phenylcarbonamido-thiocarbohydrazide, thus:

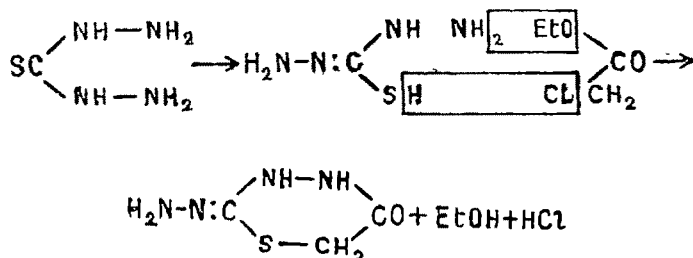


Stolle and Bowles (Ber., 41, 1101) obtained 1-amino-5-thiol-2-hydrazino-1:3:4-triazole by long and continued heating of a mixture of hydrazine hydrate and thiocarbohydrazide. If instead of the free basic compounds, an intimate mixture of their hydrochlorides are heated to 170-180°, the reaction takes an entirely different course

and there is formed 5-thio-1:2:3:4-tetrahydro-isotetrazole, thus :

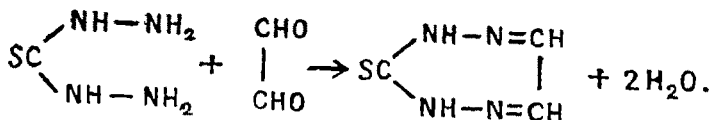


As thiocarbamide reacts with monochloroacetic acid to form pseudo-thiohydantoin, thiocarbohydrazide reacting in the pseudo form, gives a similar compound with monochloroacetic ester, thus :



2-Hydrazino-5-Keto-2, 3, 4, 5 tetrahydro-1, 3, 4 thiodiazine. The resulting compound gives a benzal derivative with benzaldehyde and possesses no mercaptanic properties.

The action of glyoxal on thiocarbohydrazide has been found to be very interesting, in as much as, a hepta-tetrazine compound is formed by the elimination of two molecules of water from molecular quantities of the reacting materials :



EXPERIMENTAL

Preparation of Dithio-p-urazine.

(a) A mixture of thiocarbohydrazide and carbondisulphide in molecular proportions was heated in presence of water in a sealed tube at 130-140° for three to four hours. After cooling white crystalline deposits were found in the

tube which were taken out and separated by filtration from the mother liquor. The solid residue was then dissolved in hot water and boiled with animal charcoal to remove the tarry matter and filtered hot. The filtrate on concentration yielded the dithio-*p*-urazine. It was recrystallised from hot water with the addition of a few drops of concentrated HCl in white rectangular plates melting at 203-204° with decomposition. The yield is almost theoretical.

(b) When a mixture of hydrazine hydrate (one molecule) and carbon disulphide (two molecules) was heated in presence of water in a sealed tube at 100° for 5-6 hours, little or no reaction took place. On raising the temperature to 140-150° the reaction came to an end in the course of 2-3 hours. The solid residue was then treated in the same way as described in (a). The yield in this case also was fairly good.

(c) A mixture of hydrazine hydrate (one molecule), alcoholic potassium hydroxide (one molecule) and carbon disulphide (two mols.) was heated in a sealed tube at 100° for four to five hours. The light brownish black solution was filtered. The filtrate was acidified with dilute HCl and again filtered and was then boiled with a small quantity of animal charcoal. The filtrate on concentration or better on the addition of a few drops of concentrated HCl, deposited white crystals of dithio-*p*-urazine. The dithio-*p*-urazine prepared according to all the above methods gave the same dibenzyl-ether (m. p. 142°C; S=19.53), the same disulphide (m. p. 218°C with decomp.; S=43.94) as described in our previous paper (Trans., 1924, 125, 1215).

Thiocarbohydrazido-thiocarbonamide.

An aqueous solution of one molecule of thiocarbonylhydrazide hydrochloride and two molecules of potassium

sulphocyanide was boiled for five hours in a flask fitted with an upright condenser. The contents of the flask while hot contained a very small quantity of a light yellow crystalline mass. The filtered solution on standing for several hours, deposited thiocarbohydrazido-thiocarbonamide in long white needles and was recrystallised from hot water; it melted at 218-219°C.

Found: N=42.38; S=38.91 per cent.

$C_2H_7N_5S_2$ requires N=42.42; S=38.78 per cent.

N-4-Amino-dithiourazole.

When thiocarbohydrazido-thiocarbonamide was heated with a few c.c.'s of strong hydrochloric acid for ten to fifteen minutes, it was converted into the hydrochloride of N-4-amino-dithiourazole. The excess of hydrochloric acid was removed by evaporation on the water bath and the remaining solution was then treated with an excess of sodium acetate solution when the free base separated out. It was then purified by crystallising from water acidified with a drop or two of hydrochloric acid. It melted at 228° with decomposition. It was readily soluble in hot water, difficultly in alcohol and insoluble in all other organic solvents.

Found: N=38.2; S=43.19 per cent.

$C_2H_4N_4S_2$ requires N=37.9; S=43.24 per cent.

The compound thus prepared gave the same benzal derivative with benzaldehyde (m. p. 136°), the same dibenzyl-thioether (m. p. 147°) and the disulphide (m. p. 214° with decomposition) as the corresponding derivatives of Arndt and Bielichs' N-4-amino-dithiourazole (*ibid*).

Thiocarbohydrazido-carbonamide.

To a solution of one molecule of thiocarbohydrazide hydrochloride was gradually added an aqueous solution of two mols. of potassium cyanate under cooling. The reaction commenced at once. The mixture was allowed

to stand for an hour and then filtered. The solid mass thus obtained, crystallised from hot water in white rectangular plates melting at 230° . The yield was extremely poor.

Found: $N = 47.02$; $S = 21.58$ per cent.

$C_2H_7ON_2S$ requires $N = 46.97$; $S = 21.47$ per cent.

N-4-Amino-thiourazole.

When thiocarbohydrazo-carbonamide was heated with concentrated hydrochloric acid for about twenty minutes, it was converted into the hydrochloride of N-4-amino-thiourazole. The solution was then treated with an excess of sodium acetate solution when the free base was liberated. It was then crystallised from water containing a little hydrochloric acid, in white needles melting at $195-196^{\circ}$ with decomposition. It is both basic and acidic in nature.

Found: $N = 42.45$ per cent.

$C_2H_4ON_4S$ requires $N = 42.42$ per cent.

The *benzal* derivative was obtained by following the same method as described in the preparation of the benzal derivative of N-4-amino-dithiourazole. It was crystallised from benzene in white needles melting at $150-151^{\circ}$.

Found: $S = 14.45$ per cent.

$C_6H_8ON_4S$ requires $S = 14.54$ per cent.

The *disulphide* was prepared in the same way as in the preparation of the corresponding derivative of N-4-amino-dithiourazole. It melted at $180-181^{\circ}C$ with decomposition. Found: $S = 24.76$ per cent; $C_2H_2ON_4S$ requires $S = 24.61$ per cent.

Thiocarbohydrazido-dicarbonyldiphenylamide.

On mixing an aqueous solution, or better, a dilute hydrochloric acid solution of one molecule of thiocarbohydrazide and two molecules of phenyl isocyanate at

the ordinary temperature, the diphenyl-dicarbonamide derivative separated in white plates. It was dissolved in sodium hydroxide solution, precipitated with hydrochloric acid and crystallised from a large quantity of boiling water. It melted at 216-217°C. Found: N=24.46 per cent. $C_{15}H_{15}O_2N_6S$ requires N=24.42 per cent.

5. Thio-1, 2, 3, 4-tetrahydro-isotetrazole.

An intimate mixture of the hydrochlorides of thiocarbohydrazide and hydrazine in molecular proportions was heated in an oil-bath at a temperature between 170-180°C for three to four hours, with frequent stirring when a semi-solid molten mass was formed which, however, solidified on cooling. The powdered mass was then extracted with glacial acetic acid and precipitated from the solution by the addition of water, as a light yellow amorphous powder, melting at 126-127°C. Found: N=55.41 per cent. CH_4N_4S requires N=53.84 per cent. From six gms. of thiocarbohydrazide hydrochloride only 0.35 gm. of the resulting product could be obtained in a pure condition.

Thiocarbohydrazide and monochloracetic ester: Formation of 2-hydrazino-5-keto-2, 3, 4, 5-tetrahydro-1, 3, 4-thiodiazine.

An alcoholic solution of one mol. of monochloracetic ester was gradually added to an alcoholic solution of thiocarbohydrazide (1 mol.) and potassium hydroxide (1 mol.), when the reaction commenced with evolution of heat and separation of a white crystalline product. After standing for about half an hour, the crystalline mass was separated by filtration and crystallised from a large quantity of water in white plates, which melted with decomposition at 220°C. Found: S=22.06 per cent. $C_3H_6ON_4S$ requires S=21.92 per cent.

The *benzal* derivative was prepared by shaking a hydrochloric acid solution of the substance with benzaldehyde when a white solid mass gradually separated. It was then crystallised from alcohol in white plates melting at 149-150°C. Found: $S=13.89$; $C_{10}H_{10}ON_4S$ requires $S=13.67$ per cent.

Thiocarbohydrazide and Glyoxal: Formation of a heptatetrazine compound.

An aqueous solution of one mol. of thiocarbohydrazide hydrochloride was boiled with one mol. of glyoxal-sodium bisulphite. The solution assumed a light brown colour and a brownish yellow precipitate was gradually formed. The heating was continued for three to four hours. After separating the solid mass by filtration, it was purified by dissolving in caustic soda solution and precipitating with hydrochloric acid. It was then crystallised from pyridine. The light brownish yellow crystalline compound thus obtained, melted at 220°C with decomposition. Found: $N=43.11$; $S=24.80$ per cent. $C_3H_4N_4S$ requires $N=43.75$, $S=24.80$ per cent.

The action of other di-aldehydes, di-ketones and diamines upon thiocarbohydrazide is under investigation and will form the subject of a subsequent communication.

Our best thanks are due to Sir P. C. RAY and Dr. J. C. Ghosh for the kind interest they have taken in the work.

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The Condensation of Resorcinol and a few other Aromatic Hydroxy Compounds with some Acids, Esters, Lactones and Lactams.

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A considerable amount of work has been done on the condensation of phenols with the anhydrides of polybasic organic acids, by Baeyer and a host of other investigators.¹

The very wide application of the reaction between phenols and acid anhydrides has established beyond doubt peculiar reactivity of the carbonyl group of the acid anhydride in giving rise to phthalein-like bodies.

A slightly different type of acid anhydride is *o*-sulpho benzoic anhydride, which was also observed by Schon to react with phenols in the same manner as phthalic anhydride (Amer. Chem. J., 1898, 20, 257). The 'sulpham' of this anhydride (benzoic sulphimide), or 'saccharin,' was also found to behave similarly. (Monnet and Koetschet, Bull. Soc. Chim., 1897, 17 (ii), 690; also Dutt, T. 1922, 121, 2389).

¹ Baeyer (Ber., 1871, 4, 658); Baeyer and Caro (Ber., 1875, 7, 968); Lunge and Burokhardt (Ber., 1884, 17, 1598; Ber 18, 2864. Silberrad, Proc. 1908, 209; Nencki and Sieber (1881, Ai, 671); (1881, A-1, 591 and 811), J. Pr. Chem. [2], 23, 147-156 and 537-550. Succino-rhodamine Ber. 23, R. 811), in more recent years, Quinolineins (Ghosh, 1919, T. 1104); Citraconeins, Shri Krishna and Pope (1921, T. 289); Camphoreins (Sircar and Dutt, 1922, T. 1288; Shri Krishna, T. 258; and Singh, Rai and Lall T. 1421 in the same year); Phenyl-succineins, Lapworth and MacRae (1922, T. 2722); Diphenesins, Dutt (1928, T. 225).

The last mentioned example suggested a study of the reactivity of the carbonyl group in configurations other than that of anhydrides. Besides the case of 'saccharin,' there are a few other instances of such in the literature. Thus, some monobasic organic acids were found by Cohn to react with resorcinol to give rise to what are known as the 'benzeins,' which are very much analogous to phthaleins (Cohn, Ber. 1892, 24, 2064). Another instance of the reactivity of the carbonyl group in giving rise to phthalein-like products, is found in Sri Krishna's work on the condensation of the lactone, coumarin with phenol and resorcin (1921, T. 1420).

The present work has for its object the further study of the reactivity of the carbonyl group specially in configurations not hitherto investigated, in respect of condensation with resorcinol and similar other aromatic hydroxy compounds. It seems that the condensation of this type between acids and phenols has not been studied sufficiently thoroughly so as to establish the generality of the reaction, while the study of the reactivity of esters, lactones and lactams (all of which contain the reactive carbonyl group), presents an almost untrodden ground.

With this object in view, typical acids of the aliphatic, aromatic and heterocyclic series, have been taken for investigation and found to give phthalein-like products with resorcin, pyrogallol, etc.

The behaviour of esters has also been examined to determine if they were more or less reactive than the acids, and it has been found that, as a rule, the esters react with greater ease than the acids from which they are derived.

As the reactivity of lactones was only indicated by Sri Krishna's work on coumarin (*loc. cit.*), more work on this line seemed desirable to establish the generality of the reaction.

The lactam, isatin has also been examined with the same object, it being found that the lactamic, or the α -carbonyl group may also be made to react with phenol, resorcinol, etc., to give products analogous to phthaleins.

A much more interesting case for study was found in the investigation whether both the carbonyl groups of the anhydrides of dibasic acids can be made to react either simultaneously or successively. This part of the work presents an entirely new aspect of the question, not having been hitherto investigated by previous workers. The present work in this direction goes to show that the reaction does not, under ordinary circumstances, take place with both the carbonyl groups simultaneously, though it is possible to make them react successively, with the same or different phenols, with good yield. Under more drastic conditions, *viz.*, heating longer at higher temperature, with larger quantity of condensing agent, it is also possible to make both the carbonyl groups of phthalic anhydride react simultaneously with resorcinol, though the yield of the desired product is rather small.

The results of the present investigation are briefly as follows:—

In the acid series, two hydroxy acids (salicylic and gallic) have been found to give fluoresceins when heated with resorcin in presence of zinc chloride (powdered and anhydrous), in a current of dry hydrochloric acid to 180-200°C.

Salicylic acid has been found to condense with pyrogallol as well, to give a product non-fluorescent in alkalies or organic solvents.

An amino acid, *viz.*, anthranilic acid, has been condensed with resorcin and diethyl-*m*-amido-phenol and found to give a benzein in the one case, and a rhodamine in the other. The *o*-amino-resorcinol benzein thus obtained, is found to have a fluorescence of the same kind as that of

the *o*-hydroxy compound derived from salicylic acid. Both give orange-green fluorescence in alkaline solutions which however changes to bluish-red on standing,—the change in the case of the amino-benzein taking place with greater ease. The rhodamine gives red solutions with greenfluorescence in acids and organic solvents. The effect of the substitution of amino group for hydroxyl group in the benzeins, is therefore not very marked. The presence of free amino group in the final product is proved by the isocyanide reaction and by the action of nitrous acid.

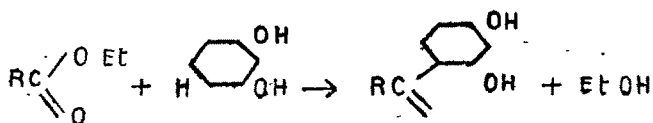
An aliphatic acid, *viz.*, stearic acid, has also been condensed with resorcin, yielding a fluorescein. Unlike the other products this is found to dissolve in benzene and less readily in ether. The compound is found to have only a moderate affinity for animal fibres. The fluorescence is also a little subdued.

Pyromucic acid, a heterocyclic acid, also gives a fluorescein with resorcin. The compound has been obtained by heating mucic acid and resorcin with zinc chloride in a current of dry hydrochloric acid. In alkaline solution the fluorescence changes from a greenish to a bluish tone on standing.

It is interesting to note that the bromine-content in the bromo derivatives of the above compounds, seems to vary according to the nature of the compound, for some of the compounds give tetra- (those derived from benzoic and salicylic acids), and some di-bromo derivatives (those from gallic and anthranilic acids), when the bromination is effected under similar conditions without taking any precautions. This is in agreement with Cohn's observations regarding similar compounds previously mentioned (*loc. cit.*).

Two esters, those of benzoic and salicylic acids, have also been examined. It is found that the reaction

between them and resorcinol, pyrogallol, etc., takes place with a greater readiness than in the case of corresponding acids. The yields are much better. The greater facility of the reaction in the case of the esters, may be plausibly explained by assuming that the first stage of the reaction consists in the elimination of a mol. of alcohol instead of a mol. of water as in the previous case,



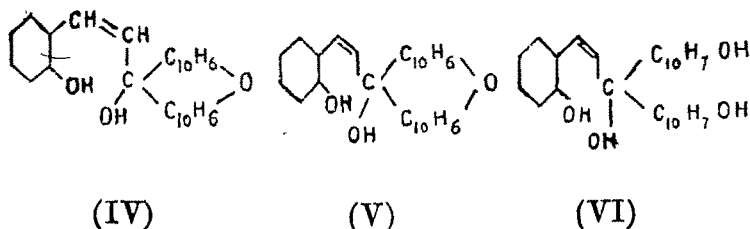
while the subsequent stages are the same in both the cases. The elimination of alcohol may be supposed to take place with greater ease than that of water.

In the study of condensation of lactones, the present work has been chiefly done on coumarin, in extension of previous work. It is found that it also gives a rhodamine (not previously prepared) with diethyl-*m*-amidophenol, which has properties analogous to true rhodamines, both in colour, dyeing properties, and solubility.

α - and β -naphthols have also been condensed with coumarin, giving rise to phthalein-like bodies. The β -naphthol compound is found to dissolve in caustic soda with strong green fluorescence. The ready solubility in alkali is explained by the non-closure of the lactone ring in the final product. This assumption is confirmed by analytical data which correspond to the structure (IV).

The α -naphthol compound, which was found extremely difficult to purify owing to tar-formation, is also slightly fluorescent in caustic soda solution, due no doubt, to partial *o*-condensation giving a fluorane-like substance (V).

The main product being α -naphthol coumarein (VI)



Complete separation could not be effected as both the products dissolve in the same solvents.

Pyrogallol has also been found to condense with coumarin to give a non-fluorescent substance of "gallein"-like nature.

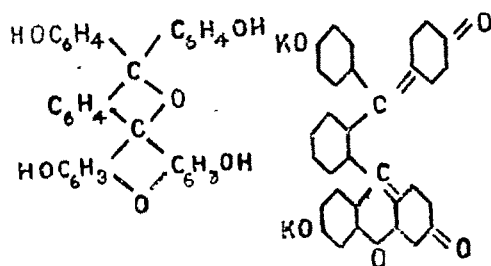
An observation that repeatedly engages the attention in the study of these condensations, is the peculiar behaviour of compounds in which pyrogallol is the second or phenolic component. It is found that all such compounds are non-fluorescent in alkaline solutions as well as in organic solvents, though the only difference between them and the resorcinol derivatives consists in the presence of additional hydroxyl groups in the former, in the *o*-positions to the pyrone-oxygen atom.

Coming at last to the study of the reactivity of both the carbonyl groups in the anhydride of dibasic acids (phthalic anhydride being chosen in the present case), the following observations were made in the course of the present work.

It was found that on heating the anhydride (one mol.) with four mols. of resorcin to 220°C with zinc chloride in a current of dry hydrochloric acid, no other product than fluorescein was obtained. Phenol-phthalein (a compound in which one of the carbonyl groups has already been acted upon), was next heated with resorcin and zinc chloride in a current of dry hydrochloric acid to $180\text{--}200^{\circ}\text{C}$. Curiously enough, it was found that fluorescein was

formed under the circumstances as previously observed by Meyer and Pfotenhauer (Ber., 1905, 38, 3958).

Phenol-phthalein was then heated with an excess of resorcin (about 2.5 mols.) with a larger quantity of zinc chloride in a current of dry hydrochloric acid to 220°C, for five hours. Under these conditions the desired condensation was effected, and on purification the product was found to be an extremely interesting compound in which both the carbonyl groups of the anhydride were acted upon, the first with phenol, and the second with resorcinol mols. It is thus a compound which contains both a phenol-phthalein and a fluorescein component. The constitution (VII) is given to this compound.



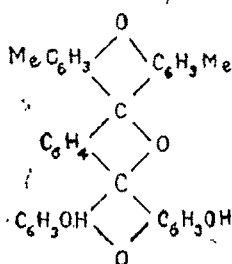
(VII)

(VIII)

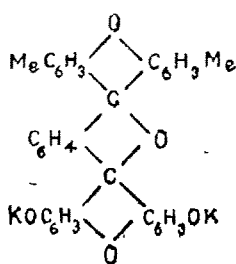
It dissolves in alkalis and organic solvents with an intense green fluorescence in no way inferior to that of fluorescein itself. It gives a tetrabromo derivative corresponding to eosin and a di-potassium salt, formulated as in (VIII). The compound is thus doubly quinonoid. The intensity of the colour and fluorescence is no doubt ascribable to 'double symmetric tautomerism,' which it is obviously capable of exhibiting.

The compound may also be regarded as being formed by the condensation of one of the carbonyl groups of phthalic acid with two mols. of phenol, and of the other carbonyl group with two mols. of resorcinol.

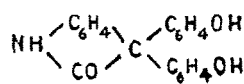
To confirm the reactivity of the second carbonyl group of phthaleins, *p*-cresol-phthalein anhydride was prepared according to Drewsen (A. 212, 340-47) by heating phthalic anhydride (one mol.) and *p*-cresol (two mols.) with conc. sulphuric acid. The compound was chosen in preference to *o*-phenol-phthalein anhydride, as the latter is difficult to prepare in any quantity. The anhydride chosen is interesting also in having a pyrone-ring already formed in the molecule. The product of condensation of the anhydride with resorcin, is found to dissolve with less ease in alkalis and to give a solution, the fluorescence of which is less bright than that of fluorescein, being more red and less orange on dilution than fluorescein. The difference is no doubt ascribable to the increased complexity of the mol., and to the presence of methyl groups in *p*-positions to the pyrone-oxygen. It is given the constitution (IX), the potassium salt having the constitution (X).



(IX)



(X)



(XI)

Fluorescein itself when heated with excess of (3 mols.) resorcin, with excess of zinc chloride in a current of dry hydrochloric acid to 230-40°C for 6 to 7 hours, was found to give a product, which unlike fluorescein, is insoluble in sodium carbonate and precipitated by carbon dioxide from solutions in caustic soda. On purification, this gives a solution in caustic soda, the fluorescence of which is somewhat subdued, and much less bright than that of

fluorescein itself. Analytical results agree with the compound expected.

The last three condensations may be classed with those of the lactones, as the first components in these reactions are compounds of the lactone type. Looked at from this point of view it is hardly surprising that these condensations should be possible, though it must be admitted that they take place under conditions more drastic than in any other case hitherto studied. The heaviness and complexity of the molecules sufficiently explain the difference.

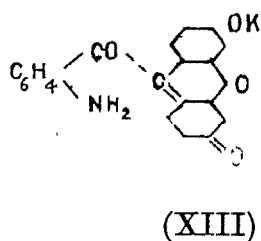
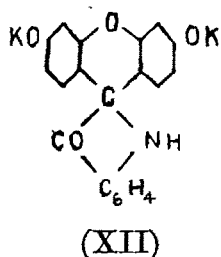
In the lactam series, only one lactam, *viz.*, isatin, has been studied. It was found by Baeyer and Lazarus (Ber. 18, 2637-43), to condense with phenol, toluene, anisole and di-methylaniline in presence of conc. sulphuric acid at ordinary temperatures, the condensation taking place with the β -carbonyl group of isatin.

In connection with the present investigation, phenol and isatin were heated with conc. sulphuric acid to 120-30°C for 6 to 7 hours, but the product was identical with "phenol-isatin" obtained by Baeyer to which he gave the constitution (XI).

In the present work, isatin has also been condensed with phenol in the presence of zinc chloride at 180-90°C. The product is found to dissolve in caustic soda with red colour much deeper than that of alkaline solutions of 'phenol-isatin,' and produces no colour effect in alkaline solution by the addition of potassium ferrocyanide while 'phenol-isatin,' under similar conditions gives a violet colour. The difference between the two compounds is ascribed to the condensations having taken place with the α -carbonyl group in one case and with the β -carbonyl group in the other.

Isatin has also been found to condense with resorcin, in the presence of zinc chloride in a current of dry hydrochloric acid giving a product analogous to fluorescein.

Diethyl-*m*-amidophenol also condenses to give a rhodamine. The resorcin compound gives a di-potassium salt which probably has the constitution (XII)



In this compound, it is interesting to find that though no quinonoid form is possible under ordinary conditions, yet it is fluorescent and coloured. The fluorescence is however slight in alkaline solution, though marked in conc. sulphuric acid solution. By assuming that the lactam-ring is broken by hydrolysis, quinonoid form (XIII) becomes possible. This however does not explain the existence of the di-potassium salt.

The following further experiments have been made to establish whether the α - or the β - carbonyl group of isatin reacted in these compounds.

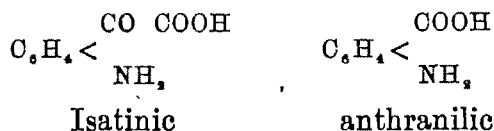
(1) Both isatin, and 'phenol-isatin,' as well as the present products liberate nitrogen with nitrous acid.

(2) With chloroform and alcoholic potash isatin and also 'phenol-isatin' are unaffected. The present products react vigorously with the reagents, and the smell of isocyanide slowly develops in the mixture on standing. This may be due to the breach in the lactam ring by hydrolysis, and formation of a free amido group.

(3) Both 'phenol-isatin' and the present products are insoluble in sodium carbonate and precipitated by carbon-dioxide from solution in caustic soda probably because under ordinary conditions the lactam ring is unaffected.

The difference in behaviour in isocyanide-reaction may be ascribed to the fact that while in 'phenol-isatin' the

β -carbonyl group of isatin was reactive, in the present products, the α -(or the true lactamic) carbonyl group reacts with phenol, resorcin, diethyl-*m*-amidophenol and also pyrogallol, rendering the lactamic ring unstable, and readily opened by alcoholic caustic potash setting free the amido group. In fact, the present compounds may be looked upon as being derived from isatinic acid in the same manner as the amino-benzein (already described), is derived from anthranilic acid,—the two acids being comparable.



Pyrogallol has also been found to condense readily with isatin yielding a product, similar to other pyrogallol derivatives, which gives deeply coloured non-fluorescent solutions in alkalis and organic solvents.

p-Cresol has also been condensed with isatin, giving a product insoluble in acids and alkalies, but dissolving readily in glacial acetic acid and conc. sulphuric acid in the latter solvent with slight fluorescence. Its properties are therefore analogous to those of *p*-cresolphthalan anhydride.

EXPERIMENTAL.

General observations.

The following observations may be made regarding the general procedure followed in the preparation of the compounds described in this paper.

One mol. of the acid, ester, lactone, or lactam was heated with two mols. of resorcin, pyrogallol, etc., with powdered anhydrous zinc chloride to 180-200°C, for three to four hours, generally in a current of dry hydrochloric acid. The cases in which this method was departed from is noted under the individual preparations. No

hydrochloric acid gas was used in the preparation of the rhodamines.

The purification of the compounds was effected by powdering the crude product wherever possible, extracting with boiling solution of dilute hydrochloric acid to remove zinc chloride, dissolving the washed residue in dil. caustic soda solution, and precipitating with dil. acetic acid or hydrochloric acid. This operation was repeated two or three times when necessary, and the washed and dried residue crystallized from alcohol, acetone or pyridine as the case might be. In some cases hydrochloric acid precipitated the product in a resinous form from alkaline solutions, in which cases dil. acetic acid was employed instead. In cases where the product was not sufficiently purified by precipitation, it was boiled with animal charcoal in alcoholic solution, and the filtered solution poured into water and then the washed residue crystallized from alcohol, etc.

In some cases, the removal of zinc chloride proved to be a matter of considerable difficulty, and the purification was effected by repeated extraction with hot dil. hydrochloric acid solution, both in the first stage, and in the subsequent stages. In these cases the final purification was effected from acetone.

Bromination was effected by adding slight excess of bromine to an alcoholic solution of the product, and allowing to stand overnight. The ppt. was filtered, washed with hot water, dissolved in caustic soda, precipitated with hydrochloric acid and finally crystallized from alcohol. As mentioned previously, in some cases di-, and in others tetra-bromo derivatives were thus obtained.

The potassium salts were prepared by suspending the finely powdered substance in hot water, adding a slightly less than the theoretical quantity of caustic potash (purified by extraction with absolute alcohol) and

constantly stirring the mixture heated on the water-bath, till solution was complete. It was filtered from the excess of the substance and the filtrate evaporated to dryness on the water-bath. It was then powdered, washed with absolute alcohol, and then extracted with the minimum quantity of water, and the aqueous solution concentrated, when the potassium salt separated.

Only two benzoyl derivatives, those of the salicylic acid and the phenol-phthalein compounds, were prepared by the usual method. As these derivatives contain nearly the same percentage of carbon and hydrogen as the parent substances, and as particularly it was practically impossible in many cases, to distinguish between the mono- or poly-benzoylated products by combustion results, this class of derivatives were not prepared in the case of other compounds.

The rhodamines were generally formed at somewhat lower temps. and less heating was required for their formation. For purification, they were powdered, extracted repeatedly with hot water and hot dil. caustic soda to remove zinc chloride and dissolved in hot dil. hydrochloric acid and precipitated with caustic soda or ammonium hydroxide. This was repeated and the dried product purified from alcohol, acetone or pyridine. In cases of difficulty of purification, the alcoholic solution was boiled with animal charcoal, and the filtered solution was poured into water till a turbidity was produced. The solution was then filtered and allowed to stand overnight with more water. The ppt. which separated was then purified by crystallisation from alcohol, etc.

THE CONDENSATIONS WITH ACIDS. (A)

1. *Resorcinol-gallein*.—3.5 gms. of gallic acid and 4.5 gms. of resorcin were heated on the oil-bath till the mixture melted (at about 200°C). At this stage, the flame

was removed, and 3 gms. of zinc chloride were added in small quantities at a time. A vigorous reaction ensued, and the mixture completely melted. The temp. was lowered to 190°C and kept there till the vigour of the reaction subsided. Afterwards the temp. was raised to 200°C and kept there for 3 hours. All this time, a slow current of hydrochloric acid gas was passed over the mixture.

The purification was effected by the general method. Yield 80% of the theoretical. It is a dark-red powder dissolving in alkalis and organic solvents with deep green-red fluorescence. Soluble in alcohol, more so in acetone, insoluble in acetic acid, ether and benzene. Dyes wool and silk brownish shades deepening on chroming. It does not melt up to 250°C . It gives a red di-bromo derivative.

Found: $\text{C}=67.7, 67.72\%$; $\text{H}=3.96, 4.02\%$. $\text{C}_{19}\text{H}_{12}\text{O}_6$ requires $\text{C}=67.85\%$, $\text{H}=3.6\%$.

Di-bromo derivative—is a red powder, giving red solution in alkali without fluorescence. Dyes wool and silk deep red. It does not melt up to 250°C .

Found: $\text{Br}=31.97\%$. $\text{C}_{19}\text{H}_{10}\text{O}_6\text{Br}_2$ requires $\text{Br}=32.4\%$.

2. *Resorcinol-o-amino-benzein*.—4 gms. of anthranilic acid and 6.8 gms. of resorcin were mixed with 5 gms. of zinc chloride and heated for 4 hours to 180°C in a current of dry hydrochloric acid. Purification was effected as in the case of 'resorcinol salicylein.' (Sen and Sinha, Amer. Chem. J., 1923, 12, 2984.) It was finally crystallized from alcohol and dried in the vacuum desiccator. Yield about 70% of the theoretical. The substance closely resembles resorcinol salicylein in colour, fluorescence, solubilities and dyeing properties. It softens at 175.77°C . It gives a di-bromo, and a mono-potassium derivative.

Found: $\text{N}=4.36\%$, 4.41% . $\text{C}_{19}\text{H}_{13}\text{O}_5\text{N}$ requires $\text{N}=4.6\%$.

Di-bromo derivative.—Closely resembles the bromo-derivative of resorcinol salicylein in properties. Dyes red shades. Decomposes at 195°C . Found: $\text{Br} = 34.4\%$. $\text{C}_{19}\text{H}_{17}\text{O}_3\text{NBr}_2$ requires $\text{Br} = 34.7\%$.

Mono-potassium derivative.—Dissolves in water with green-red fluorescence changing to bluish-red on standing. Found: $\text{K} = 11.6\%$. $\text{C}_{19}\text{H}_{12}\text{O}_3\text{NK}$ requires $\text{K} = 11.4\%$.

3. *Resorcinol-stearic acid*.—3 gms. of stearic acid (1 mol.), were mixed with 3.5 gms. (3 mols.), of resorcin and heated with the addition of 3 gms. of zinc chloride to $200\text{--}210^{\circ}\text{C}$ for $4\frac{1}{2}$ hours. A large excess of resorcin was employed to prevent the presence of unaltered stearic acid in the final product. To ensure the completion of the reaction the heating was effected for a longer time than usual at a higher temp.

The product was purified by the general method, and finally from benzene. It was dried in the vacuum desiccator. Unlike the other products it was soluble in benzene and to a less extent in ether. The fluorescence was slight but appreciable, and the colour deep red. On standing a bluish tone is assumed. The product has very slight affinity for wool and silk. It softens at 152°C .

Found: $\text{C} = 79.78, 79.70\%$. $\text{H} = 9.5, 9.48\%$. $\text{C}_{30}\text{H}_{42}\text{O}_3$ requires $\text{C} = 80\%$, $\text{H} = 9.33\%$.

4. *Resorcinol-pyrömuicein*.—4 gms. of mucic acid and 4 gms. of resorcinol were gradually heated with 4 gms. of zinc chloride in a current of dry hydrochloric acid. At 140°C a vigorous reaction ensued. When it subsided a little, the temp. was gradually raised to 200°C and kept there for $3\frac{1}{2}$ hours. Purification was effected by the general method. Finally from pyridine. The product is similar to the stearic acid compound in colour and fluorescence, but has more pronounced dyeing properties. It is however insoluble in benzene or ether, and not very soluble in alcohol.

The fluorescence is also slight. It does not melt up to 250°C.

Found: C=73.0%, H=3.9%. $C_{17}H_{10}O_4$ requires C=73.37%, H=3.6%.

5. *Pyrogallol-salicylein*.—3 gms. of salicylic acid and 5 gms. of pyrogallol were heated with 3.5 gms. of zinc chloride for 4 hours to 180-90°C. Purification was effected by the general method. Finally from a mixture of pyridine and water (2:1). The alkaline solution has a deep red-brown colour, without fluorescence, as also solutions in organic solvents. It is not very soluble in alcohol, but dissolves in acetone, and a mixture of pyridine and water. It does not melt up to 250°C.

Found: C=67.6%, H=3.82%. $C_{19}H_{11}O_6$ requires C=67.85%, H=3.57%.

6. *Anthranilo-rhodamine*.—3 gms. (slight excess of 1 mol.) of anthranilic acid and 6.5 gms. of di-ethyl-*m*-amido phenol were finely ground together and heated on the oil-bath till the mixture melted. Powdered zinc chloride was added in small quantities with constant stirring. The mixture was then gradually heated to 180°C for 3 hours, till the melt solidified. The cold mass was finely powdered, extracted repeatedly with hot water and hot dil. caustic soda to remove zinc chloride. It was then dissolved in warm dil. hydrochloric acid and precipitated with ammonium hydroxide or caustic soda. This was repeated and the washed residue finally purified from alcohol and obtained in the form of a pink powder. It dissolves readily in acids with green-red fluorescence, more marked in organic solvents. Yield about 60% of the theoretical. It softens at about 230°C. Dyes wool and silk an impure violet shade (with a mixture of green).

Found: N=9.56, 9.62%. $C_{27}H_{23}O_2N_3$ requires N=9.74%.

CONDENSATIONS WITH ESTERS. (B)

7. *Resorcinol-salicylein*.—A mixture of 3 gms. of methyl salicylate and 4.5 gms. of resorcin was heated with zinc chloride with an air-condenser in a current of dry hydrochloric acid. The temp. was raised gradually to 200°C and kept there for 4 hours. The purification was effected by the method for the identical product obtained from the acid. Finally purified from acetone. Yield 85% of the theoretical. Does not melt up to 260°C.

Found: C=74.84%, 74.86%; H=4.38, 4.3%. $C_{19}H_{13}O_4$ requires C=75.0%, H=4.0%.

8. *Pyrogallol-salicylein*.—3 gms. of oil of winter-green and 5 gms. of pyrogallol were heated with 4 gms. of zinc chloride in a current of dry hydrochloric acid for 4 hours with an air-condenser. The product was identical with that obtained from the acid. Yield about 85% of the theoretical.

Found: C=67.64%, H=3.72%. $C_{19}H_{12}O_6$ requires C=67.85%, H=3.57%.

CONDENSATIONS WITH LACTONES. (C)

9. *β -Naphthol-coumारेin*.—A mixture of 3 gms. of coumarin and 6 gms. of β -naphthol was heated for 4 hours at 180-90°C in a current of dry hydrochloric acid, together with 4 gms. of zinc chloride. The product was extracted repeatedly with boiling dil. hydrochloric acid solution to remove zinc chloride, washed with hot water, extracted with caustic soda and the solution ptd. with dil. acetic acid solution (hydrochloric acid threw down the substance in a pasty form). The operation was repeated twice. After each precipitation the ppt. was boiled with dil. hydrochloric acid to remove traces of zinc chloride the removal of which was found difficult to accomplish. Purified first from boiling alcohol containing animal charcoal, and then from acetone. (A portion of the

crude product was left after first extraction with caustic soda solution, but was not further investigated.) It was dried in the vacuum desiccator. It is a yellowish brown powder not very soluble in alcohol, but dissolves in acetone, glacial acetic acid and conc. sulphuric acid with green fluorescence. It is pptd. by carbon dioxide from alkaline solution. It softens at 115°C . It has very feeble affinity for animal fibres.

Found: $\text{C}=83.56, 83.4\%$; $\text{H}=5.2, 4.8\%$. $\text{C}_{20}\text{H}_{18}\text{O}_2$, H_2O , or $\text{C}_{20}\text{H}_{20}\text{O}_3$ requires $\text{C}=83.65\%$, $\text{H}=4.8\%$.

10. *α -Naphthol-coumarein*.—3 gms. of coumarin and 6 gms. of α -naphthol were heated with 4 gms. of zinc chloride in a current of dry hydrochloric acid for 3 hours to 180°C . There was a great deal of tar formation, which reduced the yield to 40% of the theoretical. After preliminary precipitations as in the case of the β -naphthol compound, the product was dissolved in alcohol, and boiled with animal charcoal for 10 minutes. The cooled filtrate was poured into water till a turbidity was produced. It was filtered and the filtrate allowed to stand overnight with more water. The ppt. thus obtained was finally purified from acetone and dried in a vacuum desiccator. It is a dark brown powder dissolving in caustic soda with red colour. It softens at about 117°C . It has no appreciable affinity for animal fibres.

Found: $\text{C}=80.38, 80.02\%$; $\text{H}=4.89, 4.9\%$. $\text{C}_{20}\text{H}_{20}\text{O}_4$ requires $\text{C}=80.18\%$, $\text{H}=5.07\%$.

13. *Pyrogallol-coumarein*.—3 gms. of coumarin were heated with 5 gms. of pyrogallol and 3 gms. of zinc chloride to $180\text{--}90^{\circ}\text{C}$ for 4 hours in a current of dry hydrochloric acid. The product was analogous in properties to other pyrogallol derivatives and purified by analogous method. Finally from alcohol. It does not melt up to 250°C .

Found : $C=66.2\%$, $H=4.16\%$. $C_{21}H_{13}O_6, H_2O$ requires $C=66.49\%$, $H=3.96\%$.

14. *Coumarin-rhodamine*.—3 gms. of coumarin and 7 gms. of diethyl-*m*-amido phenol were heated with 3 gms. of zinc chloride to $180-90^\circ C$ for 3 hours, till the melt completely solidified. The purification was effected as in the case of 'anthranilo-rhodamine.' Only the alcoholic solution was boiled with animal charcoal and to the cool filtrate, water was added till a turbidity was produced. It was filtered, and the filtrate allowed to stand with more water. The ppt. thrown down was filtered, and finally purified from acetone. It dissolves in acids with a violet colour, and greenish fluorescence, more marked in organic solvents. Softens at $156^\circ C$. Dyes wool and silk violet shades.

Found : $N=6.16, 6.2\%$. $C_{23}H_{22}O_4N_2$ requires $N=6.36\%$.

15. *Phenol-resorcinol-phthalein*.—6.5 gms. (1 mol.) of phenol-phthalein, and 5.5 gms. ($2\frac{1}{2}$ mols.) of resorcin, were heated with 5 gms. of zinc chloride to $210-15^\circ C$ for $4\frac{1}{2}$ hours. Purified by the general method. Finally from alcohol. Yield 70% of the theoretical. It is an orange powder somewhat soluble in hot water, more so in acetone, alcohol. The alkaline solution shows a fluorescence of the same nature and degree as fluorescein. It does not melt up to $250^\circ C$. It gives a tetra-bromo, and a di-potassium, and a di-benzoyl derivative. Dyes a greenish yellow shade.

Found : $C=76.23, 76.30\%$, $H=4.38, 4.52\%$, $C_{32}H_{12}O_8$ requires $C=76.47\%$, $H=4.4\%$.

Tetra-bromo derivative.—Orange powder dissolving in alkalis with some fluorescence. Dyes wool and silk red shades. It does not melt up to $250^\circ C$. Found : $Br=39.3\%$. $C_{32}H_{18}O_8Br_4$ requires $Br=39.1\%$.

Di-potassium derivative.—Found : $K=13.9\%$. $C_{32}H_{18}O_8K_2$ requires $K=13.8\%$.

Di-benzoyl derivative.—Melts at 156-58°C. Found: C=77.5%, H=4.4%. $C_{48}H_{30}O_8$ requires C=77.74%, H=4.22%.

15A. *Fluorescein*.—3.2 gms. of phenol-phthalein were heated with 2.5 gms. of resorcin, with 2.5 gms. of zinc chloride for 3 to 4 hours to 180-200°C. The purification was effected by the general method. Finally crystallized from alcohol. It has all the properties of fluorescein.

Found: C=72.36%, H=4.0%. Fluorescein, $C_{20}H_{12}O_5$ requires C=72.3%, H=3.7%.

16. *Resorcinol-p-cresolphthalein*.—3.3 gms. of *p*-cresolphthalein anhydride and 2.5 gms. of resorcin were heated together with zinc chloride to 200-220°C for 4½ hours in a current of dry hydrochloric acid. It was purified by the general method, finally from acetone. It is a red powder, soluble in caustic soda with green-red fluorescence less bright than that of fluorescein. It is precipitated by carbon dioxide from this solution. Soluble in acetone and pyridine, less soluble in alcohol. Softens at about 220°C. Gives a di-potassium derivative.

Found: C=79.36, 79.42%; H=5.0, 4.92%. $C_{34}H_{24}O_6$ requires C=79.68%, H=4.67%.

Di-potassium derivative.—Found: K=12.9%. $C_{34}H_{22}O_5K_2$ requires K=13.2%.

17. *Resorcinol-fluorescein*.—3.5 gms. (1 mol.) of fluorescein, and 3.5 gms. (3 mols.) of resorcin, were heated together with 4 gms. of zinc chloride for 5 hours to 230-40°C. The purification was effected, after removal of zinc chloride by extracting the product with sodium carbonate solution to remove unchanged fluorescein. It was then washed, dissolved in caustic soda and pptd. with carbon dioxide. It was re-dissolved in caustic soda pptd. by hydrochloric acid, dried, and purified finally from a mixture of pyridine and water (2:1). The product unlike

fluorescein is insoluble in sodium carbonate. Alkaline solutions have a fluorescence less bright than that of fluorescein. It decomposes at about 230°C.

Found: C=73.86, 73.93% ; H=3.84, 3.86%. $C_{32}H_{20}O_7$ requires C=74.4%, H=3.87%. Fluorescein requires C=72.2%, H=3.7%.

CONDENSATIONS WITH LACTAMS. (D)

18. *Resorcinol-isatinein*.—3 gms. of isatin and 4.5 gms. of resorcin were heated for 3 hours with zinc chloride to 180-90°C, in current of dry hydrochloric acid. The purification was effected by the general method. Finally from alcohol. Yield about 75% of the theoretical. It is an orange powder, dissolving in alkalis with slight fluorescence, more marked in conc. sulphuric acid solution. Does not melt up to 265°C. It dyes wool and silk orange shades from an acid bath. It gives a di-potassium and a tetrabromo derivative.

Found: N=3.84, 3.98%. $C_{20}H_{13}O_4N$ requires N=4.2%.

Di-potassium derivative.—Found: K=19.5%. $C_{20}H_{11}O_4K_2N$ requires K=19.2%.

Tetra-bromo derivative.—Dyes red shades. Decomposes at 230°C. Found: Br=49.7%. $C_{20}H_9O_4NBr_4$ requires Br=49.4%.

19. *Isatin-rhodamine*.—3 gms. of isatin and 6.5 gms. of diethyl-*m*-amido phenol were heated with 4.5 gms. of zinc chloride for 3 hours to 180°C. The purification was effected as in the case of the anthranilic acid compound. Finally from acetone. Dissolves in acids with a green-red fluorescence. It softens at 242°C. It dyes wool and silk an impure violet shade.

Found: N=9.3, 9.2%. $C_{28}H_{31}O_2N_3$ requires N=9.5%.

20. *Pyrogallol-isatinein*.—3.5 gms. of isatin and 6 gms. of pyrogallol were heated with 4 gms. of zinc chloride

for 3 hours to 180°C. Purification was effected by the general method. Finally from acetone. It has properties similar to other pyrogallol derivatives, giving non-fluorescent deeply coloured solutions in alkalis and organic solvents. Does not melt up to 250°C.

Found: $N=3.7$, 3.74% . $C_{20}H_{18}O_8N$ requires $N=3.86\%$.

21. *Phenol-isatinein*.—3.5 gms. of isatin and 3 gms. of phenol were heated with 4 gms. of zinc chloride for 4 hours to 190°C. The product was steam-distilled and the residue purified by the usual method. Finally from alcohol. The product is a greyish powder dissolving in alkalis with a red colour. It softens at about 285°C.

Found: $N=4.2$, 4.24% . $C_{20}H_{18}O_5N$ requires $N=4.41\%$.

22. *p-Cresol-isatinein anhydride*.—3.5 gms. of isatin and 5.5 gms. of *p*-cresol were heated together with 4 gms. of zinc chloride in a current of dry hydrochloric acid for $2\frac{1}{2}$ hours at 180°C. The product after removal of zinc chloride was extracted with glacial acetic acid and the solution poured into water. The ppt. was filtered, washed and crystallized from glacial acetic acid. Obtained as a greyish powder. Dissolves readily in acetic acid and in conc. sulphuric acid with faint fluorescence. Does not melt up to 250°C.

Found: $N=4.0\%$. $C_{22}H_{17}O_2N$ requires $N=4.28\%$.

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Electro-osmotic Experiments on Intensity of Adsorption of a Constituent Ion by an Insoluble Salt.

Part I.

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A heteropolar precipitate like that of an insoluble salt has a tendency to adsorb its constituent ions from aqueous solutions. It seems that this type of adsorption is responsible for several phenomena which do not at first sight appear to be correlated. Lottermoser observed that precipitated silver salts pass into the colloidal state when the solution contains one of the common ions in excess. The charge of the colloid is of the same sign as that of the constituent ion which is present in excess in the solution. Marc from his experiments on the adsorption by crystalline surfaces [*Z. phys. Chem.*, 75, 710 (1911); 81, 641 (1913)] concluded that a crystalline substance adsorbs only those dissolved substances which can form isomorphous compounds with the crystal or compounds which have similar crystalline forms. Fajans and Beer [*Ber.*, 46, 3486 (1913); also 48, 700 (1915)] pointed out that the separation of a radio-element from its solution by an insoluble salt takes place only when the radio-element itself can form an insoluble precipitate. Paneth and Horowitz [*(Z. Phys. Chem.* 89, 513, (1915); also

Phys. Z. 15, 924 (1914)] recognised in view of Marc's work that the separation of radio-elements, by precipitates is due to the adsorption of the radio-element, and that a radio-element will be adsorbed by an insoluble heteropolar adsorbent only when it can form an insoluble salt. Paneth however, considers that the adsorption of the radio-element consists in an actual exchange of places between ions in the crystal lattice and the radio-elements in solution. Thus barium ions in barium sulphate are replaced by radium ions from solution and the barium ions pass into solution.

It has been pointed out by the writer that in the case of a large number of colloidal suspensoids, the stabilising electrolyte has an ion in common with the colloid, and that the adsorption of a common ion by a precipitate is a simple consequence of the modern view of the structure of crystals of salts. (Far. Soc. Disc. October, 1920; published October, 1921.) The adsorption of an ion imparts a charge to the surface and thus tends to peptise the precipitate. It has been further pointed out (Mukherjee, *loc. cit.*; Phil. Mag., 1922, VI, 44, p. 327) that there is an essential difference in the manner of adsorption as pictured by Paneth and that which must be assumed to account for the stability of colloids. The type of adsorption suggested by Paneth will not impart a charge to the surface and hence cannot account either for the observations on the charge of colloids in the presence of peptising electrolytes or for their stability. The exchange of ions between the crystal lattice and the solution must be a slow process, when the salt is only sparingly soluble, whereas the adsorption of ions by the surface will be much quicker. Both types of adsorption have probably to be taken into account, but it appears

from the literature on colloids that the adsorption of ions as such by the surface is more frequent than an actual interchange of ions as conceived by Paneth. Experimental evidence will be adduced in the sequel in support of this view.

Another class of phenomena is also probably closely connected with the adsorption of constituent ions by a precipitate. Bradford [(*Biochem. J.*; 10, p. 169 (1916), 11, p. 14 (1917)] has suggested that the adsorption of the precipitating ions is at least partly responsible for the formation of Liesegang rings. The adsorption of constituent ions may also affect the permeability of the precipitate to the diffusing ions—a factor which also probably plays an important role in the formation of Liesegang rings. (Fischer, *Koll. Zeit.* 30, 1920, p. 13.)

The experiments of Debye and Scherrer have shown that colloidal particles have the same crystalline structure as they have in large masses or well-developed crystals. One has, of course, to remember that the surface forces acting on constituent ions existing in the solution are not exactly similar to those acting on the ion in the interior of the lattice. (Madelung, *Phys. Z.* 20, 494, 1919). But such considerations do not materially affect the validity of our point of view.

Fajans and Beckerath (*Z. Phys. Chem.* 97, 1921, 4/8) have suggested an explanation similar to ours regarding the adsorption of a constituent ion by a crystal lattice. They have further attempted to consider the energy required to separate an adsorbed ion from the surface in the light of the work necessary to separate the constituent ions from the crystal lattice and the energy change due to hydration. These authors consider that there is a close relationship between the

intensity of adsorption of the ions by the surface and the solubility of the corresponding salt (*loc. cit.*, p. 500). Langmuir (J. Amer. Chem. Soc. 38 (1916) 2221; 39, 1917, 1848), considers the intensity of adsorption to be determined by the energy changes associated with the process. So far no very definite result has been obtained from this treatment as the energy changes associated with the process of adsorption do not admit of easy theoretical calculation and the estimates of the energy change are based on more or less arbitrary assumptions. It would appear from the sequel that Fajans's method of treatment is too simple to account for the intensity of adsorption of ions.

The present investigation deals with the adsorption of ions by precipitated and carefully washed lead chromate. This substance was selected because it has been used in many cases for the investigation of Liesegang rings. Moreover there is a large number of insoluble lead salts and it is of interest to compare the relative intensity of adsorption of different anions by a surface of lead chromate with the solubility products of the corresponding salt.

The amounts of ions adsorbed has been mostly measured from chemical analysis, or from measurements of activity where the sensitive radio-active methods can be used. These methods do not give any indication as to whether the adsorbed ions replace those of the same sign in the crystal lattice thus leaving the crystal and its surface electrically neutral or are adsorbed on the surface with or without exchange of ions and the surface becomes electrically charged, through an excess in the adsorption of ions of one sign. Electro-osmotic measurements can decide between these two possibilities. Moreover, it is more convenient and accurate than analytical methods. It may be noted here that recently several investigators

have emphasised the necessity of considering simultaneous adsorption of the solvent and of the solute. The analytical result represents the net effect. One cannot therefore simply say that so much of the solute has been adsorbed. In fact some assumptions about the relative adsorptions of the solute and the solvent have to be made in order that an actual idea of the adsorption of the solute can be made (*cf.* Wo. Ostwald and Izagguire, *Koll. Z.* 30, 1919, 279, also previous literature). Of course it is possible that for the dilute solutions with which we are dealing, the adsorption of the solvent can be assumed to be more or less constant. But if there be alterations in hydration, on the adsorption of ions consequent on the variation in the electric charge, then we have a fresh source of disturbance and analytical data do not give a clear idea of the adsorption.

EXPERIMENTAL.

The arrangement used for the electro-osmotic measurements is a modified form of that used by Briggs the straight tube being replaced by a U-tube which does away with the use of porous plugs or glasswool (*cf.* Mukherjee, *Nature*, Dec. 2, 1922). The method gives results accurate within $\pm 7\%$. The position of the electrodes in the U-tube did not vary during these experiments. The same U-tube and the glass tube connections were used throughout these experiments. The U-tube was always filled with the precipitated lead chromate between two marks symmetrically placed one on each limb of the U-tube. The precipitate was stirred with water or electrolyte and then poured in the U-tube and allowed to settle for 24 hours. The excess of lead chromate was drawn off with a pipette. The thickness of the layer of the precipitate was 12.8 cm. The preparation

and purification of the precipitate requires great care. Chemically pure lead nitrate was further purified by recrystallisations. The crystals were powdered and dried at 102° . Chemically pure potassium chromate was carefully washed in a Buchner funnel. Two solutions of lead nitrate and potassium chromate of equal strength were prepared and lead-chromate was precipitated by addition of equivalent amounts of the two solutions from a burette into a beaker with silver nitrate as outside indicator.

The supernatant liquid was poured out and the precipitate was digested in pure boiling water for half an hour and the supernatant liquid was again poured out. The finer particles were removed along with the supernatant liquid. The process was repeated 10-12 times. It appears that potassium chromate was adsorbed in perceptible quantities during the precipitation, though the supernatant liquid after precipitation showed no trace of chromate with silver nitrate. During the first two digestions, the supernatant liquid assumed a yellow colour after some time, but in subsequent washings remained quite colourless. The substance becomes more free from adsorbed chemicals with repeated digestions. The digested and wet lead chromate was kept in stoppered resistance glass bottles in a place free from fumes.

Differences in the size of the air bubble within fair limits do not influence its velocity for the same experimental arrangement.

Every experiment was carried out under exactly similar conditions. The electric current is switched on for five minutes and the tube is then allowed to rest till the air-bubble becomes stationary, and the distance the bubble has moved is noted. The direction of the current is then reversed, and the mean of the two readings is taken. This was repeated at least five times in each case and their

mean was taken. The different readings do not differ by more than $\pm 5\%$.

When electrolytes were used, the same amount of the precipitate was washed with the electrolyte solution several times to ensure that the concentration of electrolyte taken remains unchanged after removal of the water and after adsorption. The results are given below. The method is not free from certain sources of error and it is intended to investigate them with a view to modify the experimental arrangements. It may be added that the usual method is sufficiently accurate for our present purpose.

At high electrolyte concentrations the acids set free on electrolysis of the salt solution convert the chromate into dichromate with the consequent change in colour.

The velocity of the bubble is proportional to the density of the electrical charge on the surface. Since

$$v = \frac{e \cdot H \cdot q \cdot \delta}{\eta}$$

where v = velocity in cms/sec (of the bubble).

H = pot. grad ent.

q = sectional area.

e = density of electrical charge; δ = the thickness of the double layer and η = co-efficient of viscosity.

H and q are constant under the conditions of the experiment. η may be taken to be constant for these dilute salt solutions, and δ is assumed to be constant.

* We have taken the usual form of the equation cf. (Freundlich, *Kapillarchemie*, 1922, p. 328).

TABLE I.

*Lead Chromate.*Velocity in cm. per sec. $\times 300$.

Electrolytic conc.	Water.	KCl.	K ₂ CrO ₄ .	Pb(NO ₃) ₂ .	KNO ₃ .	K ₂ SO ₄ .	BaCl ₂ .	KI.	KIO ₃ .	CaCl ₂ .
O	18.2
N/15000	...	22.0
N/5000	...	23.0	25.1	7.1	20.2	22.6	20.2	22.7	26.6	21.4
N/4000	...	26.6
N/2500	...	28.1
N/2000	...	29.8	35.8	-3	31.8	32	20.7	30.5	32.5	25.5
N/1000	...	32.4	44.9	-7.9	32.8	38.5	17.5	Decom- position sets in	36.3	25.5
N/500	...	36.8	14.3	
N/250	...	Decomposition sets in		

DISCUSSION.

The readings with water alone show that the substance is negatively charged in contact with water. We are not sure whether the negative charge owes its origin to the adsorption of chromate ions which probably could not be removed even after 13 digestions with pure boiling water, or to the adsorption of hydroxyl ions from water.* It will be seen from the above that of the four cations, K, Ba, Pb and Ca, only Pb⁺⁺ ions materially affect the velocity of the bubble, diminishing it markedly at as low a concentration as n/5000 and at a higher concentration n/1000, the bubble moves in the opposite direction.

* The question will be dealt with in a second communication.

These experiments bring out undoubtedly that the adsorption of the positively charged lead ion at first decreases the density of the negative charge on the surface till at a higher concentration, the surface positively becomes charged being covered with an excess of lead ions. It would have been of great interest to follow the the increase in charges still further with increasing concentration, but the transformation of chromate unfortunately prevents further observation.

The marked adsorption of the lead ions in contrast to that of the other cations can be readily understood if we remember that it is a constituent ion of the precipitate (*cf.* Mukherjee, Far. Soc. Disc. Oct. 1922 ; Phil. Mag., *loc. cit.*).

A comparison of the effects of K, Ba or Ca will show that for the same anion, Ba⁺⁺ ions are more adsorbed than Ca⁺⁺ ions and that K⁺ ions are least adsorbed.

On the other hand, of the anions the chromate which is the other constituent ion has a great effect on the charge. In general, on the addition of an electrolyte other than the lead salt, there is an increase in the negative charge to begin with. In the case of BaCl₂ the charge at first remains constant up to a concentration of N/2000 and then begins to decrease. This is a very common feature of the curves between the charge and the concentration of the electrolyte, when the oppositely charged ion is weakly adsorbed (*cf.* Mukherjee, Phil. Mag. VI, 44, 1922, pp. 328 *et. seq.*). In the case of CaCl₂ the anion effect predominates within the limits of concentration studied, the density of the charge being always greater than that with pure water. The cation effect is however apparent if we compare the relative

effects of calcium chloride, potassium nitrate and potassium chloride.

A quantitative comparison of the relative intensities of adsorption of individual ions is not easy. The observations show that adsorption of both ions at these low concentrations has to be considered. For the different potassium salts it is permissible to compare the relative anion effects, as the cation is the same in each case. In comparing the intensities of the adsorption of the anions, the valency of the anion has to be taken into account. For the same increase in the density of the negative charge, the *amount* of an anion adsorbed is inversely proportional to its valency. Since we know the valency and the increase in the densities of the charge compared to that for pure water, we can compare the relative amounts of the different anions adsorbed. Such a comparison is however not free from objections. First of all, the assumption (*loc. cit.*) of a constant thickness of the double layer is not certainly self-evident. Secondly, we do not know exactly the source of the charge of the surface in contact with water and a replacement of the ions already existing on the surface by the ions of the same charge present in the solution, will not alter the charge and will escape detection. Consequently, even if adsorption takes place there may be no alteration in the charge. The error due to this cause will however be smaller, when the change in charge is great. For this reason, we have taken the values at $0.0005N$ for comparison. Probably the initial charge is due to the adsorption of chromate ions as it is almost impossible to remove the last traces of adsorbed electrolytes by washing or by digestion with boiling water in many cases. The only other source may be the adsorption of hydroxyl

ions from water. Lastly the variation in the charge is due to the adsorption of two ions of opposite sign and it is evidently erroneous to refer all of the observed difference to the adsorption of one ion only. These objections are not likely to influence the general nature of the conclusions we have drawn from the comparison outlined above. Since we have at present no idea as to what determines the thickness of the double layer, we might leave it out of account, though it is probable that the thickness of the double layer depends on the density of the electrical charge. This is justifiable to some extent on the ground, that so far conclusions drawn from the assumption, that the velocity of electro-osmosis, or cataphoresis is proportional to the density of the electrical charge on the surface, have helped us consistently to explain colloidal phenomena associated with electrical charge of particles. Regarding the last objection we might neglect the adsorption of the weakly adsorbed ion, in comparison to that of the other as a first approximation, as the great change in the charge shows the preponderating effect of the one over that of the other. In order to form an idea of the relative intensity of adsorption, we must compare the amounts of the anions adsorbed at the same gm. anion concentration. The difference in the velocity is proportional to the net amount of positive or negative charge adsorbed in the form of ions (of both sign) per unit surface. If we compare the potassium salts, we may assume the adsorption of the cation to be constant and the increase in the velocity (*i. e.* of the negative charge) is then proportional to the number of ions adsorbed, multiplied by its valency. The amount of the different anions adsorbed is then given by the increase in velocity (referred to the value for water) divided by the valency of the anion. The following table shows

the values for a concentration of $\cdot 0005$ gm. anion per litre.

TABLE II.

Potassium Salts.

Anions.	Conc. in gm. ions per litre.	Difference in velocity	Valency	Amount adsorbed
Cl'	$\cdot 0005$	29.8-18.2	1	11.6
NO' ₃	$\cdot 0005$	31.3-18.2	1	13.1
SO'' ₄	$\cdot 0005$	38.5-18.2	2	$\frac{20.3}{2} = 10.15$
CrO'' ₄	$\cdot 0005$	44.9-18.2	2	$\frac{26.7}{2} = 13.35$
I'	$\cdot 0005$	30.5-18.2	1	12.3
IO' ₃	$\cdot 0005$	32.5-18.2	1	14.3

The anions arrange themselves in the following order:—

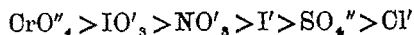


The order given above does not exactly represent the *relative* intensities of adsorption for anions of different valency. The adsorption of chromate and sulphate ions must be greater than that indicated above for two reasons.

(1) Now the velocity of osmosis indicates the net negative charge being the actual charge due to the adsorbed anions less the charge due to the fixed layer of cations. Since we are comparing equal gram-anion concentrations, the concentration of cation will be double for the divalent anions of what it is for univalent anions. The adsorption of the cations is not negligible and the amount of cation adsorbed at the higher concentration will be greater. So that the same velocity

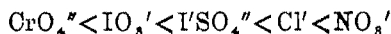
of movement of the bubble at equal gram-anion concentration would indicate a higher adsorption of divalent anions than of univalent anions, or in other words more chromate and sulphate ions are actually adsorbed than are represented by the figures 13.35 and 10.15.

(2) Secondly the density of the negative charge (44.9) for chromate ion is much greater than that in the case of iodate ions (32.5) and the greater negative charge diminishes to a greater extent the number of collision of the anions on the charge. The adsorption of an ion depends on the intensity of adsorption, *i.e.*, on the energy change associated with the process of adsorption by a neutral surface and on the number of collisions on the surface. In the case where we are dealing with the adsorption of ions, carrying an electrical charge of the same sign as that of the adsorbing surface, the number of collisions evidently do not depend on the concentration of the anion. Only those ions can strike on the surface which have sufficient kinetic energy to overcome the electrical repulsion when it approaches the surface. The greater, the negative charge of the surface, the fewer the collisions of the anion on the surface as compared to the probable number of collisions if the surface were neutral. The greater negative charge of the solid in contact with potassium chromate makes the further adsorption of chromate ions more difficult than in the case of the iodate ions of the same gram-anion concentration. If the electrical conditions were identical, the adsorption of the chromate ions would have been greater than that indicated above. We may therefore take the order to be



which is also the order of the increasing solubilities of the

lead salts expressed in terms of gr. atomic concentration of lead,



with the exception of the nitrate.

A strict comparison between the order of adsorbability and of solubility is therefore not possible. Further solubility of the corresponding salt is not a measure of the change in energy when an ion passes from the adsorbed layer in the surface to the solution. For the same reason, a comparison of the lattice energy and of the intensity of adsorption is also not possible without further assumptions regarding the energy of hydration and regarding the effect of adsorption on the hydration of the ion and on the hydration of the surface (Fajans, *loc. cit.*). We, therefore think that Fajans's conclusions as to the relationship between solubility and intensity of adsorption are untenable. It is however remarkable that the order for the other anions is practically the same as that suggested by Fajans.

SUMMARY AND CONCLUSIONS.

It is possible to draw certain definite conclusions from the experiments recorded here.

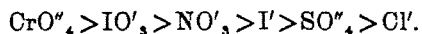
(1) A well-digested precipitate of lead chromate is not electrically neutral against water. The negative charge is probably due to the adsorption of chromate ions or in the alternative hydroxyl ions from water or of both. If the latter view were true, we may observe "hydrolytic adsorption" if the hydrogen ions in the second layer can be replaced by a cation from a neutral solution of a salt *e.g.*, sodium chloride we will have an acid extract.

- (2) The order of adsorbability of the cations is



The adsorbability of lead ions is the strongest amongst the cations. It is also very probable that besides the lattice energy of the ions, there are other factors such as the energy of hydration of the surface or of the ion which determine the intensity of adsorption, *i.e.*, the work necessary to separate an ion from the surface to the interior of the solution.

- (3) The order of adsorption of anions is probably



The adsorption of chromate is probably the strongest.

(4) The constituent ions of a precipitate are very strongly adsorbed by it. Lead ions being so largely adsorbed as to reverse the charge. This observation suggests the possibility of preparing electrically neutral precipitates. As pointed out above, experiments with electrically neutral lead chromate will enable us to have a better idea of the intensity of adsorption of the different ions. The great intensity of adsorption of the constituent ions is in agreement with the views set forth in a previous paper.

(5) It is of great interest to note that the adsorption of the constituent ions does not consist simply in the exchange of an ion in the crystal lattice with an ion in the solution, as assumed by Paneth. Ions are actually fixed on the surface imparting a charge to it and the type of adsorption considered by Paneth cannot explain the observations recorded here.

(6) Fajans's suggestion that there is a parallelism between the intensity of adsorption of an ion and the solubility of the salt of the adsorbed ion and the ion

with opposite sign in the precipitate is not tenable as the nitrate ion is adsorbed more strongly than the iodide or sulphate.

The method of treatment developed here is capable of other interesting applications.

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(*Recd. Aug. 2, 1924*)

The Electrode Potential of Mercury against its Ions in Aqueous (1) Methyl Alcohol, (2) Acetone and (3) Pyridine.

BY

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AND

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Numerous investigations have been carried out in aqueous solutions on electrocapillary phenomena since the Lippmann Helmholtz theory was developed ; but they are rare in mixed solvents and excepting the researches of Krummreich (Z. F. Electrochem. 19, 622, 1913) on aqueous ethyl alcohol, not very carefully done either. The importance of finding out how the absolute potential of metals against their ions changes with the nature of the solvent is obvious. The method which gives the most satisfactory results in this field, is the determination of the maximum position of the electrocapillary curve, and in order that the data obtained may be reliable, the conditions postulated in the Lippmann Helmholtz original equations must be fulfilled

$$dU = Edq + \gamma dS \quad \dots (1)$$

$$dq = XdS + S \frac{\partial X}{\partial E} \cdot dE \quad \dots (2)$$

$$X = \partial E$$

Where U = change in internal energy; γ = surface tension,

X=density of electrification, S=area of capillary surface, E=potential difference at the boundary, dq=quantity of electricity and c=Capacity of Unit area of the double layer.

Then only a true parabola is obtained represented by the equation

$$\gamma = \gamma_{max} - \frac{1}{2}CE^2$$

the maximum of surface tension corresponding to zero value of electrode potential. The experimental conditions in this investigation, were always so determined by trial, that the curves approximated to an ideal parabola, indicating thereby, that the primary processes at the electrode surface contemplated by Lippmann and Helmholtz, have not been accompanied by uncertain disturbing factors.

EXPERIMENTAL PRECAUTIONS.

Clark (Trans. Roy. Soc. Canada, 14, Ser. 3, Sect. 3, 73, 1921) maintains that the wet surface at the capillary is enormously greater than the cross-sectional area of the capillary due to the electrolyte creeping in between the glass walls of the capillary and the mercury column, and that the area of the wet surface never remains constant. Hence C' the capacity of the double layer at the capillary surface does not remain constant in course of experiment, and a true parabolic curve is therefore out of the question.

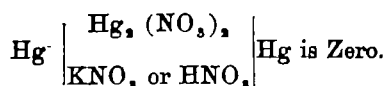
In our experiments the capillary was made perfectly dry and clean, filled completely with mercury and then dipped into the electrolytic solutions. The glass wall beneath the capillary meniscus was therefore completely dry; the motion of the mercury column due to electric charge, and its re-adjustment to final level due to external

pressure changes were too slow to leave behind a wet surface, enclosed between glass wall and mercury, which could be observed by the microscope. Only when the applied E. M. F. exceeded 1.6 volts, or the mercury column was, for some reason or other very sticky, a wet film between mercury and glass could be observed. For a capillary electrometer prepared with due precaution and used with care, it may be stated that the area of the capillary surface remains constant.

The nature of the electrocapillary curve depends a good deal on the ions, other than the mercurous ion, introduced into the solution, in order that the liquid may be sufficiently conducting. Thus Kruger and Krumreich (Z. F. Electro chem. 19, 617, 1913) found that an ideal parabola is obtained very easily when an aqueous solution of normal potassium nitrate and 0.1N $\text{Hg}_2(\text{NO}_3)_2$ was used. It is unfortunate that potassium nitrate is not soluble in non-aqueous solvents, and this important property of potassium nitrate could not be taken advantage of in these investigations. Lithium nitrate, which is soluble in the solvents used by us, did not give a parabolic curve even in pure water, though the maximum obtained was quite sharp. The same difficulty was found in the case of potassium nitrate solutions. An aqueous solution of nitric acid (0.0035N) and mercurous nitrate (0.002N) gave a fairly good parabolic curve with the maximum at 1.05 volt. The expectation that mixed solvents having similar concentrations of nitric acid and mercurous nitrate would give approximate parabolas has been realised. It appears that the absorption of ions by mercury surface has considerable influence on electrocapillary processes.

It takes a very long time for conditions of equilibrium to be established at the capillary junction in these mixed

solvents. In aqueous solution of KNO_3 and $\text{Hg}_2(\text{NO}_3)_2$, it takes not more than 15 minutes for the mercury meniscus to become absolutely stationary; but in these experiments, it was discovered, that for half an hour after starting the polarising current, the movement of the mercury meniscus was comparatively rapid, but after that interval there was an imperceptible change which continued for a very long time. The curves given below have been plotted, from readings taken after the polarising current has passed through the capillary electrometer for five to eight hours. An explanation of this long time necessary for the attainment of equilibrium can be attempted from the standpoint of "Reststrom Polarisation." The E. M. F. of a cell of the type—



If a very slight current is passed through the circuit mercury will dissolve at the anode as Hg_2^+ ion and will be deposited at the cathode from the solution. For small values of applied voltage, the back E. M. F. of polarisation will be entirely due to changes in the concentration of the mercurous ion in the liquid layer immediately surrounding the electrodes. If however, the surface of the mercury anode is very large compared with that of the cathode, as in the capillary electrometer, we are justified, in considering that for small current, the anode film does not undergo any change in the concentration of the Hg_2^+ ion. In fact, measurements of the anode potential of our capillary electrometers, showed that this was the case. Therefore, the back E. M. F. of polarisation

$$= \frac{RT}{nF} \log \frac{C}{C_0}$$

where C_0 is the concentration of Hg_2^{++} ion in the bulk of the solution which is the same as that of the anode, and C_c is the concentration of Hg_2^{++} ion at cathode film. Obviously when C_c becomes so small, that the osmotic pressure of Hg_2^{++} ion is equal to the electrolytic solution pressure of mercury, then we have an electrode at zero potential. In the stationary state, where to maintain a definite value of polarisation, a definite residual current is necessary, there must be coming as many Hg_2^{++} ion from the bulk of the solution into the cathode layer by diffusion, as are being discharged. This number in gram equivalent—

$$N = \frac{1}{86,400} \cdot \frac{D.O.}{a} \cdot \frac{C_0 - C_c}{\delta}$$

(Nernst & Merriam *Z. F. Phys. Chem.* 53, 235, 1905.)

D = Velocity of diffusion ; O = area of the cathode surface ; a = electro-chemical equivalent and δ the thickness of the diffusion layer. For the enormous polarisation that we are dealing with in the case of the capillary electrometer, C_c will be infinitely small, and—

$$\frac{i}{96,540} = N = \frac{D.O.}{a} \cdot \frac{C_0}{\delta}$$

In an actual experiment with the capillary electrometer, the residual current was found to be 4.2×10^{-8} amperes, for an area of capillary surface = .0025. Taking $D = .0023 \times M$ (M = molecular conductivity of the Hg_2^{++} ion), δ comes out to be 10^{-3} cm. approximately.

This order of magnitude for δ is the same as that obtained by Nernst and Merriam and thus it is established beyond doubt that we are here dealing with the phenomena of Reststrom Polarisation.

A considerable time might elapse before the concentration gradient across the diffusion layer $\frac{C_0 - C_1}{\delta}$ attains equilibrium conditions and then again there exist the disturbing effects produced by the movement of the mercury meniscus in response to continuous change in surface tension. This will specially be the case, when the mercury surface in the capillary, becomes negatively charged, for that condition will correspond to inconceivably low value of C_1 .

It is satisfactory to note, that the electrocapillary curves obtained, when these precautions were taken, were approximate parabolas. See Figs. I and II.

EXPERIMENTAL PROCEDURE.

A Wolff Dial Potentiometer standardised by the Reichsantalt was connected to a 4-volt battery, and any required E. M. F. was applied through a galvanometer; the exact value of the E. M. F. being obtained by reference to a standard Weston element. The sensitiveness of the galvanometer in the circuit being known, the strength of the residual current corresponding to a definite polarising voltage can be ascertained. The capillary tube was cleaned before each experiment by washing with strong nitric acid and keeping under chromic acid overnight. It was washed finally with conductivity water, dried in a current of dust-free air, and filled with redistilled mercury. It was then immersed in the electrolytic solution. The U-tube capillary electrometer was found to have an advantage over the vertical tube ending in a capillary, in that, it was more stable. The position of the mercury meniscus was read off as usual with a reading microscope and the difference between the levels

of the mercury column in the manometer and in the capillary was measured by means of a travelling microscope capable of reading height to $\frac{1}{1000}$ cm. For capillaries of large bore, an adjustable mercury reservoir was not necessary, the difference in the levels of the mercury columns in the instrument itself was measured directly, the variation in the diameter of the capillary tubing along its length being too small in this case, to be taken into account. A large number of capillary electrometers were prepared, and only those were selected, which gave easily an ideal curve with an aqueous KNO_3 , $\text{Hg}_2(\text{NO}_3)_2$ solution.

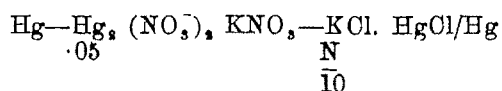
The back E. M. F. of the polarised capillary surface is always less than the applied voltage by an amount equal to $i \times R$ where R is the resistance of the circuit and i the strength of the residual current. The resistance of the circuit is primarily due to the galvanometer and to the electrolytic solution in the capillary lying above the mercury meniscus. It is impossible to measure directly the magnitude of this resistance, but it is easily calculated from the following data: (1) galvanometer resistance, (2) bore of the capillary and length of the column of electrolyte, and (3) specific resistance of the solution. It was found that in no case, the correction in back E. M. F. due to this factor exceeded 1 millivolt.

Pyridine, acetone and methyl alcohol used in this investigation were obtained from Kahlbaum and distilled in the laboratory until constant boiling points were obtained.

EXPERIMENTAL RESULTS AND DISCUSSION.

The experimental results are given in Figs. I and II and in Tables 2, 3 and 4.

The electrocapillary curve for aqueous solution ought to have been almost identical with that obtained by Kruger and Krumreich (*loc. cit.*). They obtained a maximum at .8 volt approximately while our experiments give a maximum at 1.005 volt. Ley and Heimbücker (*Z. F. Electrochem.* 10, 301, 1904) found that the cell



had an E. M. F. of .391 volt. Decinormal calomel element has a value of .612 volt as obtained from innumerable electrocapillary data. The maximum therefore should lie at (.612 + .391) or 1.03 volt in agreement with our results. If Kruger and Krumreich's value were true, decinormal calomel element would have an electrode potential of .412 volt, which is a move in the direction suggested by Billitzer's data, obtained from the observation of the movement of metal wires dipped in salt solution (*Ann. der. Phys.* 11, 902, 1903). Unfortunately their results could not be confirmed.

Tables 2, 3 and 4 give the electromotive forces corresponding to maximum of surface tension in mixed solvents of water-methyl alcohol, water-acetone and water-pyridine, containing mercurous nitrate and nitric acid as electrolytes. The influence of the concentration of the Hg_2^{2+} ion on the magnitude of the electrode potential is comparatively small. For the same concentration of mercurous nitrate in the various solvents, it can be shown on the basis of Walden's empirical generalisation,—for the same value of $D \sqrt{v}$, the degree of dissociation is the same,—that the relative concentration of Hg_2^{2+} ion in these solvents does not vary beyond the ratio 2 : 1.

The above values may therefore be accepted as the electrode potential of mercury against $\frac{N}{100}$ mercurous ion in the respective solvents. Table 1 reproduces the data of Krumreich (*loc. cit.*) in aqueous ethyl alcohol solution of potassium nitrate and mercurous nitrate. The results are, as has been noted before systematically about .2 volts less than the generally accepted values.

TABLE 1.
Water-Ethyl Alcohol.

Electrode Potential.	Composition by weight in per cent.	Dielectric constant D.	$\frac{E}{D}$
.778	0%	81	.95
.628	10%	75	.84
.604	30%	60	1.0
.479	50%	48.5	.97
.451	70%	38.1	1.12

TABLE 2.
Water-Methyl Alcohol.

	Composition by vol. in per cent.		
1.04 (Krumreich's value .778)	0%	81	1.20 (.95)
.719	10%	77	.93
.611	20%	72	.95
.636	30%	68	.92
.581	40%	68.5	.92
	50%	58.0	.94

TABLE 3.
Water-acetone.

Electrode Potential.	Composition by vol. in per cent.	Dielectric constant.	$\frac{E}{D}$
1.05	0%	81	1.2
.906	10%	77	1.18
.620	20%	72.5	p
.855	30%	67.5	1.25
.775	40%	62.0	1.25
.751	50%	55.0	1.36
.732	60%	48.0	1.51

TABLE 4.
Water-pyridine.

Electrode Potential.	Composition by vol. in per cent.	Dielectric constant.	$\frac{E}{D}$
1.05	0%	81	1.25
.550	10%	74	.75
.498	20%	68.3	.73
.450	30%	60	.75
.412	40%	53	.77
.388	50%	44	.90

The values of dielectric constants in Tables 1, 2, and 3 are calculated from data given in Landolt's Tabellen. The dielectric constants in aqueous pyridine given above are not very accurate and are taken from the work of Ghosh (J. C. S., 117, 1390, 1920). The fourth columns in the tables give the ratio of the electrode potential as

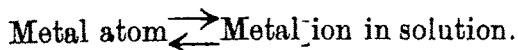
determined from the maximum of the capillary curve, to the dielectric constant of the solvents. It will be noticed that in aqueous ethyl alcohol solution the electrode potential of mercury is proportional to the dielectric constant of the solvent up to 50% of alcohol. Thereafter the ratio of $\frac{E}{D}$ increases.

In aqueous methyl alcohol, the same constancy in the value of $\frac{E}{D}$ is observed. This ratio varies about the mean value, .93, and if we accept Kruger's data for pure water as solvent, $\frac{E}{D}$ for water also has approximately the same value, *viz.*, .95.

In aqueous acetone, results obtained with 20% acetone are very peculiar in that abnormally low value of electrode potentials is obtained. With this exception, the ratio $\frac{E}{D}$ remains constant up to 40% acetone and thereafter increases as in the case of aqueous ethyl alcohol.

There is a very large drop in the value of the electrode potential as pyridine is added to water. Further addition of pyridine beyond 10% by volume, produces a slow gradual change in the value of electrode potential and we find that the ratio $\frac{E}{D}$ remains practically constant within the range 10-40% pyridine. Thereafter $\frac{E}{D}$ increases as in the case of the other mixed solvents.

The electromotive force at the boundary between a metal and its ions in solution is a measure of the free energy A of the process:



$$\text{for } E \cdot \times F = A.$$

On the reasonable assumption that the free energy of the atom of an element in the metallic state remains constant at constant temperature, this investigation points to the conclusion, that at 30° , *the free energy of mercurous ion in the above mixed solvents is within a certain range directly proportional to the dielectric constant of the solvent.*

DACCA UNIVERSITY,

[Received Oct. 25, 1924.]

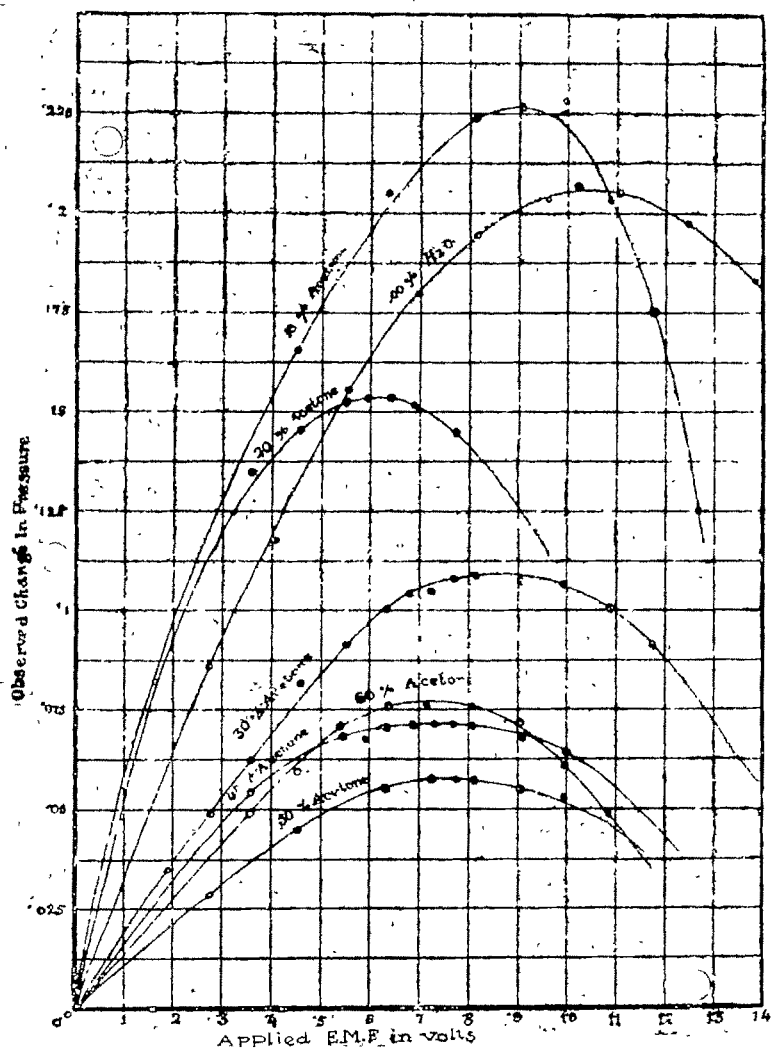


Fig. I.

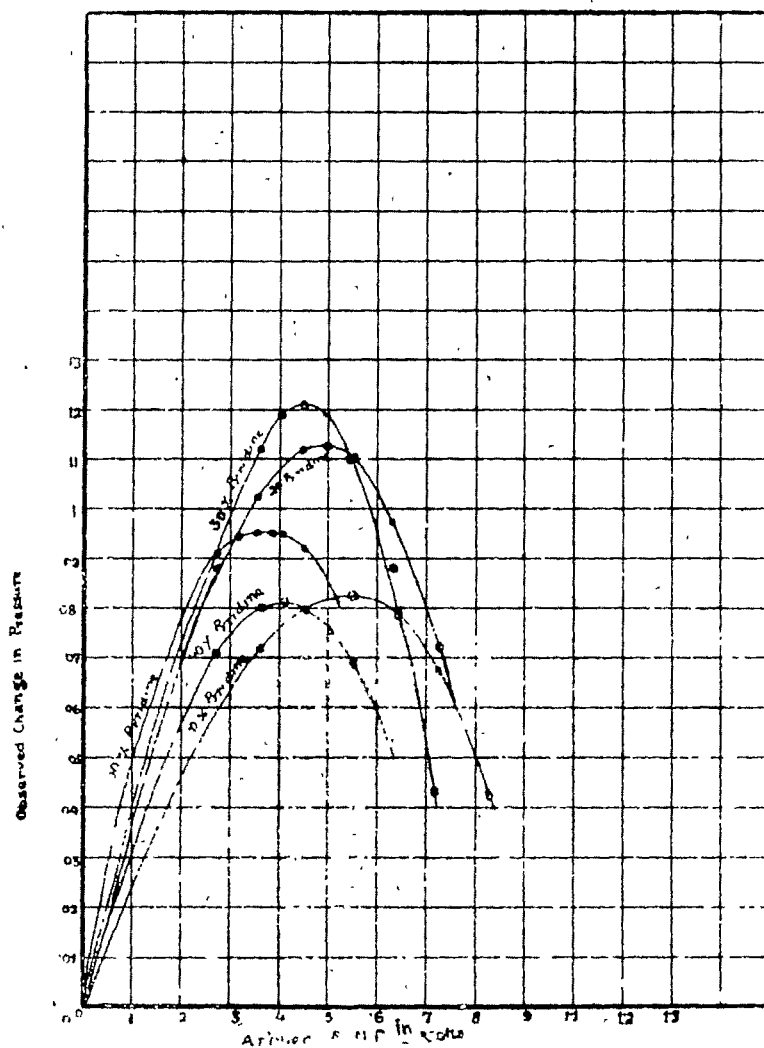


Fig. II.

Dyes derived from Phenanthraquinone.

Part V.

Phenanthraphenazinazines.

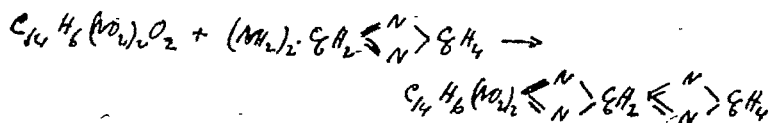
BY

ANUKUL CHANDRA SIRCAR

AND

PARESH CHANDRA DUTT.

In continuation of the work of Sircar and Dutt (J. C. S. T., 1922, 121, 1944), Sircar and Sircar (J. C. S. T., 1923, 123, 1559) and Sircar and Roy (J. C. S. T., 1924, 125, 543), this investigation was undertaken with the object of finding out if the colours of the phenanthraphenazines (Watson and Dutt, J. C. S. T., 1921, 119, 1211) could be deepened specially towards blue and green, by the introduction of an additional chromophoric azine ring in their molecules. Some phenanthraphenazinazines have now been prepared by condensing 2:3-diamido-phenazine (Ullmann and Manthner. B., 35, 4302) with phenanthraquinone and its derivatives.



These compounds all contain two azine rings in their molecules and are very suitable for comparing with the

* The first four papers of this series have appeared in the Journal of the Chemical Society of London (T. 1922, p. 1944 *et seq.*; T. 1923, p. 1559; T. 1924, p. 543).

corresponding compounds containing only one azine ring (Watson and Dutt, *loc. cit.*; Sircar and Dutt, *loc. cit.*).

A comparison, made below, of the colours of the dyeings on wool of a number of phenanthraphenazinazines described in this paper with those of the corresponding phenanthraphenazines (Watson and Dutt, *loc. cit.*) and phenanthranaphthazines (Sircar and Dutt, *loc. cit.*), will show that the colours of the phenanthraphenazines can be easily deepened and fuller and brighter shades obtained by the introduction of an additional heterocyclic azine ring in their molecules.

Name of the compound.	Colour of the dyeing on wool.
1. 2-amino-phenanthraphenazinazine	... Very deep brown.
2-amino-phenanthraphenazine	... Yellow.
2. 2:7-dinitrophenanthraphenazinazine	... Deep maroon.
2:7-dinitrophenanthranaphthazine	... Light yellow.
3. 2-hydroxy-phenanthraphenazinazine	... Violet-brown.
2-hydroxy-phenanthranaphthazine	... Yellow.
4. 2:7-dibromo-phenanthraphenazinazine	... Reddish-brown.
2:7-dibromo-phenanthranaphthazine	... Light yellow.

Though the phenanthraphenazinazines excel the corresponding mono-azines in so far as they dye deeper and fuller shades, the deepening of the colour is in every case towards brownish shades and none of the compounds dye in blue or green colour.

The azinazines, described in this paper, are remarkably stable substances and insoluble in the ordinary solvents. They are however soluble in pyridine. They dissolve in strong sulphuric acid with characteristic colour; water precipitates them unchanged as light, flocculent masses, well adapted for dyeing on wool (from an acid bath).

EXPERIMENTAL.

Phenanthraphenazinazine.

The precipitate produced by boiling 1.04 grams of phenanthraquinone and 1.05 grams of 2:8-diamido-phenazine

in 60 c.c. of glacial acetic acid, separated from hot pyridine, on the addition of hot water, in chocolate-coloured microscopic needles not melting below 290° . The substance dissolves in strong sulphuric acid with a violet colour and dyes wool in reddish-brown shades. (Found : $N=14.88$, $C_{28}H_{14}N_4$ requires $N=14.66$ per cent.)

For the preparation of the compounds described below, separate solutions of equimolecular quantities of the quinone and the 2:3-diamidophenazine, in glacial acetic acid, were boiled together for some time; the amorphous brownish precipitates obtained were, except where otherwise stated, purified by precipitation from hot pyridine solution by the addition of hot water. They invariably separated in an amorphous condition and could not be obtained crystalline. None of the compounds melts below 290° .

2:7-Dinitrophenanthraphenazinazine,—prepared from 2:7-dinitrophenanthraquinone (boiling for one hour), was purified by extracting for some time with a little acetic acid and precipitating the residue from pyridine. It dissolves in strong sulphuric acid with a violet colour and dyes wool in greenish-brown shades. (Found : $N=17.95$. $C_{28}H_{12}O_4N_6$ requires $N=17.80$ per cent.)

The three following compounds were purified in a similar way to the preceding one.

4:5-Dinitrophenanthraphenazinazine,—prepared from 4:5-dinitrophenanthraquinone, was obtained as a chocolate-black powder dissolving in sulphuric acid with a blue colour and dyeing chocolate shades on wool. (Found : $N=18.05$ per cent.)

2-Nitrophenanthraphenazinazine,—prepared from 2-nitrophenanthraquinone (boiling for 45 minutes), dissolves in sulphuric acid with a bluish-violet colour and dyes wool in chocolate-brown shades. The substance is

soluble in nitro-benzene or aniline. (Found: $N=16.6$. $C_{26}H_{13}O_2N_3$ requires $N=16.39$ per cent.)

4-Nitro-phenanthraphenazinazine,—resembles the 2-nitro compound in all its properties. (Found: $N=16.36$ per cent.).

2-Bromo-phenanthraphenazinazine,—prepared from 2-bromo-phenanthraquinone (boiling for half an hour), was purified by extracting for some time with acetic acid and precipitating the residue from pyridine. It was obtained as a chocolate-brown precipitate. It gave a blue colouration with sulphuric acid and dyed wool in reddish-brown shades. (Found: $N=12.31$, $C_{26}H_{13}N_4Br$ requires $N=12.15$ per cent.).

2:7-Dibromophenanthraphenazinazine,—was obtained, in the usual way as a chocolate precipitate, from 2:7-dibromophenanthraquinone (boiling for two hours). It gave with sulphuric acid a violet colouration and dyed wool in deep reddish-brown shades. (Found: $N=11.0$. $C_{26}H_{12}N_4Br_2$ requires $N=10.37$ per cent.).

Dibromophenanthraphenazinazine,—was prepared from dibromophenanthraquinone of D. R. P. 222206 (boiling for 45 minutes). It gave a blue colouration with sulphuric acid and dyed wool in reddish-brown shades. (Found; $N=11.01$ per cent.).

Dibromonitrophenanthraphenazinazine,—prepared from dibromonitrophenanthraquinone (Mukherjee and Watson, J. C. S. T., 1916, 109, 622) and obtained as a chocolate precipitate (boiling for one hour), was purified by extracting with acetic acid. Its properties are like those of the preceding compound. (Found: $N=11.82$. $C_{26}H_{11}O_2N_5Br_2$ requires $N=11.96$ per cent.).

Bromodinitrophenanthraphenazinazine,—prepared from bromodinitro-phenanthraquinone (Mukherjee and Watson, *loc. cit.*), was purified by extracting with acetic acid and then precipitated from pyridine solutions. The substance

dissolves in sulphuric acid with a bluish-violet colour and dyes wool in greenish-brown shades. (Found: $N=14.68$. $C_{26}H_{11}O_4N_5Br$ requires $N=15.24$ per cent.).

5-Bromo-4-nitro-phenanthraphenazinazine,— prepared from 5-bromo-4-nitrophenanthraquinone of m. p. $224-226^\circ$ (Mukherjee and Watson, *loc. cit.*), gave a violet colouration with sulphuric acid and dyed chocolate-brown shades on wool. (Found: $N=14.25$. $C_{26}H_{12}O_2N_5Br$ requires $N=13.83$ per cent.).

Bromo-2-nitrophenanthraphenazinazine,—was obtained as a chocolate precipitate (after two hours' boiling) from bromo-2-nitrophenanthraquinone (Mukherjee and Watson, *loc. cit.*), and purified by extracting with acetic acid. It dissolves in sulphuric acid with a blue colour and dyes wool in chocolate-brown shades. (Found: $N=14.09$ per cent.).

2-Aminophenanthraphenazinazine,—prepared from 2-amino-phenanthraquinone (boiling for 45 minutes), dissolves in sulphuric acid with a brownish black colour and dyes greenish-brown shades on wool. (Found: $N=16.75$. $C_{26}H_{15}N_5$ requires $N=17.63$ per cent.).

The hydroxy-derivatives described below were prepared by boiling molecular quantities of the quinone and the diamine in the minimum quantity of glacial acetic acid and purified by boiling with alcohol.

2:7-Dihydroxyphenanthraphenazinazine,— prepared from 2:7-dihydroxyphenanthraquinone, dissolved in sulphuric acid with a violet-black colour and dyed wool in violet-brown shades. (Found: $N=12.59$. $C_{26}H_{14}O_2N_4$ requires $N=13.52$ per cent.).

4:5-Dihydroxyphenanthraphenazinazine,—dyed chrome-mordanted and unmordanted wool in violet-brown shades. (Found: $N=12.82$ per cent.).

2-Hydroxyphenanthraphenazinazine,— was prepared from 2-hydroxyphenanthraquinone (boiling for two hours).

(Found: $N=13.62$. $C_{26}H_{14}ON_4$ requires $N=14.07$ per cent.).

4-hydroxyphenanthraphenazinazine,— prepared in a similar way to the preceding compound, was obtained as a black precipitate (Found: $N=13.29$ per cent.).

The properties of the mono-hydroxyphenanthraphenazinazines resemble those of the dihydroxy compounds.

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The Oxidation of Triethylene Tetrasulphide by means of Potassium Permanganate.

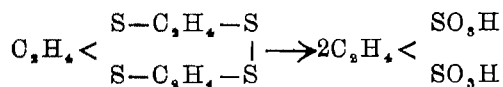
BY

SIR PRAFULLA CHANDRA RÂY.

Part I.

Oxidation with Alkaline Potassium Permanganate.

The oxidation of triethylene tetrasulphide with nitric acid has been shown to result in the break-up of the molecule with the formation of the corresponding disulphonic acid. Each of the sulphur atoms situated between a pair of carbon atoms is converted into a sulphone group while fission takes place between the two contiguous sulphur atoms with the formation of the sulphonic acid (J. C. S. Trans., 1923, 123, 2176). It seemed desirable to study the action of a less drastic oxidising agent like potassium permanganate which might be expected to yield the corresponding tetrasulphone. This expectation has been realised as will be shown below under Part II. When, however, the tetrasulphide is treated with alkaline potassium permanganate, instead of a tetrasulphone being formed, it breaks up according to the following scheme :



EXPERIMENTAL.

The tetrasulphide was suspended in water and treated with about 10 c. c. of a 3% solution of potassium permanganate and a little caustic potash solution. The

addition of the permanganate was repeated till there was a distinct excess of it. The temperature was all along kept at about 30°. The reaction was completed by finally heating on the water-bath. The mixture was cooled and the precipitated manganese peroxide brought into solution by passing sulphur dioxide. The solution was concentrated and the potassium and manganese sulphates which crystallised out were filtered off. Alcohol was next added to the concentrated liquid and the precipitate rejected. The alcohol was driven off, the residue dissolved in water and treated with barium carbonate. The precipitate was filtered off and the solution on evaporation gave crystals of the barium salt of ethylene disulphonic acid. The salt was air-dried and was found to be semi-hydrated. (Found: Ba=40.97; S=20.75.* $\text{C}_2\text{H}_4\text{S}_2\text{O}_6\text{Ba}$, $\frac{1}{2}\text{H}_2\text{O}$ requires Ba=41.02; S=19.16 per cent.).

Part II.

Oxidation with acid Potassium Permanganate.

On oxidation of the triethylene tetrasulphide with potassium permanganate in dilute sulphuric acid solution, a very interesting result is obtained. The expected sulphone formed during the reaction combines with the manganous sulphate produced and a stable double compound of the formula $[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]_2\text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ is invariably obtained. It has been found to be very sparingly soluble in the cold but dissolves readily in boiling water from which it crystallises out in the pure state. By adding

* The sulphonate was converted into sulphate by fusion with a mixture of KNO_3 and Na_2CO_3 . The 'melt' was repeatedly evaporated with conc. HCl to convert the excess of the nitrate as far as possible into the chloride. When the solution is treated with BaCl_2 a portion of the unconverted nitrate is almost invariably carried down with the BaSO_4 ; hence the p. c. of sulphur generally comes out a little too high.

barium chloride to this boiling solution, the corresponding compound with barium sulphate is at once thrown down. By a similar treatment compounds with the sulphates of calcium and strontium as also of potassium and lead have been obtained. With silver nitrate a double compound of silver sulphate is formed. Corresponding double compounds with the sulphates of nickel, cobalt, and copper have also been obtained by the addition of the respective chlorides. Peculiar interest attaches to some of these compounds, notably the combination of the sulphone with barium sulphate, as on account of its extreme insolubility all attempts to combine it with other compounds have hitherto been unsuccessful. But by following this indirect method, however, an additive compound with barium sulphate has been obtained. The sodium compound could not be isolated in a pure condition by a method analogous to that for the preparation of the potassium compound, a special procedure was therefore adopted.

In all these compounds the proportion of the respective metallic sulphate to the sulphone holds simple integral relationship. In the case of the barium compound alone the components are in the simple ratio of 1 : 1 ; whereas they are in the ratio of 2 : 3 in the manganese, copper, cobalt and nickel compounds. The ratio is as 4 : 5 in the potassium, calcium, strontium, silver and lead double compounds. The sodium compound alone gives a ratio of 4 : 1 between sodium sulphate and the sulphone.

EXPERIMENTAL.

The Oxidation of Triethylene Tetrasulphide with Acid Potassium Permanganate.—The tetrasulphide was treated with a mixture of a concentrated solution of potassium

permanganate and dilute sulphuric acid in small quantities at a time and heated on the water-bath. This process was continued till there remained a distinct excess of the permanganate. The oxidation was complete in the course of about 4 to 6 hours. The excess of permanganate was removed by passing a current of sulphur dioxide through the mixture. The solution became hot, leaving a residue of the unacted tetrasulphide, the latter was filtered off and the filtrate concentrated on the water-bath to nearly half its volume. On cooling, a colourless compound crystallised out. This was filtered, washed with cold water, and dried. (Found: Mn=7.38; S=28.86. $1\frac{1}{2}[(C_2H_4)_3S_4O_8]$, $MnSO_4$, $6H_2O$ requires Mn=7.15; S=29.13 per cent.).

Calcium Compound.—The manganese compound was dissolved in boiling water and a concentrated solution of calcium chloride added to it. A white crystalline calcium compound was at once precipitated, which was filtered and dried. (Found: Ca=7.09; C=16.81. $1\frac{1}{4}[(C_2H_4)_3S_4O_8]$, $CaSO_4$ requires Ca=7.13; C=16.04 per cent.).

Strontium Compound.—This compound was prepared by a process similar to that used for the preparation of the calcium compound. (Found: Sr=14.68; C=14.66. $1\frac{1}{4}[(C_2H_4)_3S_4O_8]$, $SrSO_4$ requires Sr=14.38; C=14.80 per cent.).

Barium Compound.—This compound was also prepared like the calcium compound. (Found: Ba=23.24; S=26.25. $[(C_2H_4)_3S_4O_8]$, $BaSO_4$, H_2O requires Ba=23.18; S=27.07 per cent.).

Lead Compound.—Lead chloride was dissolved in hot water and added to a solution of the manganese compound in boiling water. The precipitate was filtered, washed with hot water and dried. (Found: Pb=28.35. $1\frac{1}{4}[(C_2H_4)_3S_4O_8]$, $PbSO_4$ requires Pb=28.44 per cent.).

Silver Compound.—On adding a very concentrated solution of silver nitrate to a boiling solution of the manganese compound a white precipitate was at once thrown down. (Found: $\text{Ag}=29\cdot68$. $1\frac{1}{4}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$, Ag_2SO_4 requires $\text{Ag}=29\cdot31$ per cent.).

Copper, Cobalt and Nickel Compounds.—These products were obtained by adding a concentrated solution of the respective chlorides to a concentrated solution of the manganese double compound in hot water. The mixture on concentration and cooling gave crystals which were filtered, washed with a little cold water and dried. These compounds are fairly soluble in hot water. The copper compound is slightly bluish in colour. (Found: $\text{Cu}=9\cdot06$; $\text{S}=29\cdot55$. $1\frac{1}{2}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$, CuSO_4 , $4\text{H}_2\text{O}$ requires $\text{Cu}=8\cdot50$; $\text{S}=30\cdot23$ per cent.). The nickel compound is slightly greenish in colour. (Found: $\text{Ni}=8\cdot55$; $\text{S}=30\cdot03$. $1\frac{1}{2}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$, NiSO_4 , $4\text{H}_2\text{O}$ requires $\text{Ni}=7\cdot97$; $\text{S}=30\cdot40$ per cent.). The cobalt compound has a slight pink tint. (Found: $\text{Co}=8\cdot23$; $\text{S}=29\cdot28$. $1\frac{1}{2}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$, CoSO_4 , $4\text{H}_2\text{O}$ requires $\text{Co}=8\cdot00$; $\text{S}=30\cdot39$ per cent.).

The retention of the characteristic colours of the different metallic double compounds proves that the copper, nickel or cobalt atom does not form a component part of a complex.

Potassium Compound.—This compound was obtained as before by adding a concentrated solution of potassium chloride. There was no precipitate while the solution was hot, but on cooling a crystalline compound separated out. (Found: $\text{K}=12\cdot79$. $1\frac{1}{4}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$, K_2SO_4 requires $\text{K}=13\cdot02$ per cent.).

The Sodium Compound.—An aqueous solution of sodium carbonate was gradually added to a solution of the manganese compound till manganous carbonate was completely precipitated. This was filtered off and the

filtrate concentrated to a small bulk. On adding alcohol to this concentrated solution a syrup was obtained, which crystallised on keeping in a vacuum desiccator. The crystals were dissolved in water and reprecipitated with alcohol. (Found : Na=18.26; S=25.87. $\frac{1}{4}[(C_2H_4)_3S_4O_8]$, $Na_2SO_4 \cdot H_2O$ requires Na=18.77; S=26.12 per cent.).

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On Coagulation of Hydrosols by mixture of Electrolytes and Ionic Antagonism.

BY

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In a recent paper Freundlich and Scholz (*Kolloid. Chem. Beihefte*, 16, 267, 1922) have shown that the precipitating concentration of barium chloride is materially increased if the electrolyte contains in addition lithium chloride in concentrations which are not in themselves sufficient to cause coagulation. This effect has been observed with hydrosols of arseniousulphide and of sulphur prepared by Oden's method whereas for hydrosols of gold and of sulphur prepared by Weimarn's method the precipitating concentrations remain practically unaffected by such additions. It seems, as it were, the coagulating power of these cations decrease in the presence of a second cation. They found that this antagonism is very pronounced between univalent and divalent cations.

The greatest antagonism was observed between lithium and magnesium, further the effect was absent with gold sol which is not hydrated and they suggested that the effect is due to hydration of these ions and of the colloid.

Apart from considerations of hydration there are other possible factors which might account for the so-called antagonistic action of ions. It is usually assumed (though it rests on rather slender evidence cp. Mukherjee, Thesis of Doctorate of Science, University of London, 1921), that the concentrations of different electrolytes which

brings in the same rate of coagulation corresponds to a state of the colloid where the particles have the same density of electrical charge. If that view be correct the observed results might be ascribed to the following causes :—

(1) Difference in the adsorption of the anions and cations present. This is the point of view taken up by Weiser and his collaborators (*J. Phys. Chem.*, 25, 666, 1921), who consider that in the case of colloidal solutions of arsenious sulphide both the cations and anions are very largely adsorbed. Now in the mixture the anion concentration is higher than in the case of the electrolytes with a divalent cation, and there will be a greater adsorption of the anion. The negative charge on the particles is therefore greater. More cations must therefore be adsorbed to bring down the density of the electrical charge to the value which corresponds to the limiting concentrations. Weiser concludes that the higher coagulating concentration is an index of the greater amount of anion that has been adsorbed.

(2) Freundlich (*Z. Phys. Chem.*, 86, 458, 1914) has pointed out that the adsorbability of one cation may be influenced by the other that is the presence of the univalent cation in comparatively higher concentrations might interfere with the adsorption of the bivalent cation and diminish its coagulating power.

It would seem that a study of the effect of various anions on coagulation by mixed electrolytes with simultaneous determination of the electrical charge will be most useful. The electrical data are essential for a proper understanding of the nature of the effect we are studying. It is to be regretted that there is very little useful data on this subject. In this laboratory a systematic study of the electrical charge is being carried out.

The present paper deals with the effect of various

anions on coagulation of arsenious sulphide hydrosol by mixed electrolytes.*

EXPERIMENTAL.

During the last few years, a number of papers has been published showing that arsenious sulphide sol has different chemical composition, depending on the methods of preparation.

In our work, we have always adhered to the same method of preparation. The following method has been adopted for determining equi-coagulating concentrations. Light from a single filament lamp is allowed to pass through a layer of definite thickness of the coagulating colloid and the time noted when the sharp outline of the filament disappears. The intensity of the light is kept constant by passing a definite current through the filament. Electrolytes are considered to have equi-coagulating concentrations when the time required for reaching the same stage of coalescence is the same in each case. For each pair of electrolytes used the mixtures as well as the individual electrolytes are exactly equi-coagulating. During an experiment the colloid is tested from time to time by determining the coagulating concentration of a particular electrolyte.

TABLE I.

% Concentration of Sodium Benzoate.	% Concentration of Barium Chloride.	Sum.	% Concentration of Calcium Bromide.	Sum.	% Concentration of Calcium Benzoate	Sum.
0	100	100	100	100	100	100
20	134	154	159	179	175	195
33	138	171	179	212	190	223
50	180	180	170	220	180	230
65	100	166	141	207 *	148	212

* Since this work was finished Weiser has published another paper on adsorption by precipitates (J. Phys. Chem., 28, 237, 1924).

% Concentration of Sodium benzoate.	% Concentration of Magnesium chloride.	Sum.	% Concentration of Barium benzoate.	Sum.
0	100	100	100	100
20	182	202	150	170
33	203	236		
50	195	245	150	200
66	155	221	120	186

Coagulating concentration of Sodium benzoate mean—0.17 N* = 100

” ” ” Barium chloride—0.0015 N = 100

” ” ” Calcium bromide—0.0017 N = 100

” ” ” Calcium benzoate—0.0018 N = 100

” ” ” Magnesium chloride—0.002 N = 100

” ” ” Barium benzoate—0.0014 N = 100

TABLE II.

% Concentration of Sodium benzoate.	% Concentration of Potassium chloride.	Sum.	% Concentration of Lithium chloride.	Sum.
0	100	100	100	100
20	121	141	181	201
33	114	147	169	202
50	86	136	136	186
66	62	128	98	164

Coagulating concentration of sodium benzoate—0.16 N = 100

” ” ” Potassium chloride—0.06 N = 100

” ” ” Lithium chloride—0.08 N = 100

* The sum of cations given in the tables is the sum of the percentage concentration of each cation taking the coagulating concentration of each separately to be hundred.

The actual values for different pairs varied respectively from 0.166 N to 0.174 N. The difference in the coagulating concentrations of barium chloride and barium benzoate may be due to experimental errors. But nothing definite can be said until they are more carefully examined. The barium benzoate was prepared from baryta and benzoic acid.

Percentage concentration of sodium benzoate.	Percentage concentration of sodium chloride.	Sum.
0	100	100
20	141	161
33	125	158
50		
66	98	164

Coagulating concentration of sodium benzoate—0.18 N=100

" " " sodium chloride—0.08 N=100

TABLE III.

% Concentration of sodium chloride.	% Concentration of barium chloride.	Sum.	% Concentration of calcium bromide.	Sum.	% Concentration of Magnesium chloride.	Sum.
0	100	100	100	100	100	100
20	134	154	138	158	135	155
33					135	168
50	115	165	125	175	125	175
66	80	146	94	160	104	170

Coagulating concentration of sodium chloride (mean)—0.075 N=100

" " " Barium chloride—0.00155 N=100

" " " Calcium bromide—0.0017 N=100

" " " Magnesium chloride—0.002 N=100

TABLE IV.

% Concentration of sodium acetate.	% Concentration of Barium acetate.	Sum.	% Concentration of Barium chloride.	Sum.	% Concentration of Magnesium chloride.	Sum.
0	100	100	100	100	100	100
20	164	184	156	176	210	230
33	176	209	158	191	233	266
50	170	220	188	188	229	279
66	180	196	125	191	175	241

* The actual values varied from 0.073 N to 0.078 N for different pairs.

Coagulating concentration of sodium acetate (mean)—0.19 N*—100

" " " Barium chloride—0.0015 N=100

" " " Barium acetate (approx.)—0.0014 N=100

" " " Magnesium chloride—0.0019 N=100

Percentage concentration of sodium acetate.	Percentage concentration of calcium bromide.	Sum.	Percentage concentration of sodium chloride.	Sum.
0	100	100	100	100
20	191	211	178	198
38	208	241	155	188
50	204	254	121	171
66	174	240	85	151

Coagulating concentration of sodium acetate—0.18 N=100

" " " Calcium bromide—0.0016 N=100

" " " Sodium chloride—0.07 N=100

TABLE V.

Percentage concentration of Potassium Trichloroacetate.	Percentage concentration of Barium Trichloroacetate.	Sum.	Percentage concentration of Trichloroacetic acid.	Percentage concentration of Barium Trichloroacetate.	Sum.
0	100	100	0	100	100
20	123	143	20	108	128
50	100	150	33	104	137
66	85	151	66	65	131

Coagulating concentration of Trichloroacetic acid—0.04N=100

" " " Barium Trichloroacetate—0.00156N=100

" " " Potassium Trichloroacetate—0.09N=100

Percentage concentration of Barium benzoate.	Percentage concentration Barium chloride.	Sum.	Percentage concentration of $K_4Fe(CN)_6$.	Percentage concentration of KCl.	Sum.
0	100	100	0	100	100
20	78	98	20	105	125
38	64	97	33	98	126
50	49	99	50	81	131
66	33	99	66	53	119

* The actual values varied from 0.187 N to 0.195 N for different pairs.

Coagulating concentration of Barium berzoate—0.0014 N=100

" " " Barium chloride—0.0015 N=100

" " " $K_4F(CN)_6$ —0.2 N=100

" " " KCl —0.07 N=100

Percentage coagulating concentration of LiCl.	Percentage coagulating concentration of Mg Cl ₂ .*
0	100
25	200
50	220
73	233

DISCUSSION.

In their experiments neither Freundlich nor Weiser has used electrolytes other than chlorides. The question how far the adsorption of anions is responsible for the increase in the coagulating concentrations of the divalent cations remains open. They have used mixtures of electrolytes containing two cations. It has been shown by Weiser (J. Phys. Chem., 28, 1924, 241) that there is a displacement of adsorption of one cation by the other. It is therefore not clear whether the observed effect is to be attributed at least in part to the adsorption of anions or to some factor other than the adsorption of anions. If however the mixture of electrolyte contain only one cation and an increased concentration of the cation is necessary for the mixture we must conclude that anion adsorption is responsible for the effect. We have such an instance in the effect of sodium benzoate and sodium acetate on the coagulating concentration of sodium chloride. Displacement of adsorption of one cation by another is impossible since we have got only one cation.

It will be noted that sodiumacetate increases the coagulating concentration of sodium chloride almost to

* The data for the pair LiCl and MgCl₂ are taken from Freundlich's *Kapillarchemie*, p. 634 (1922), and added for comparison only.

the same extent as it does in the case of barium chloride. Similarly sodium benzoate has almost equal effects on sodium chloride and barium chloride. So we conclude that even in cases where the displacement of adsorption of one cation by another is not possible the effect of the anion is as pronounced as in the case where displacement of adsorption may occur in addition.

TABLE VI.

Percentage concentration of Lithium Chloride.	Percentage * concentration of Barium Chloride.	Percentage concentration of Sodium Acetate.	Percentage concentration of Barium Chloride.	Percentage concentration of Sodium Chloride.
0	100	0	100	100
25	183	20	156	178
50	110	33	158	155
73	110	50	138	121
		66	125	85

It is therefore difficult to say whether the effects of sodium acetate on Barium chloride is due to the displacement of the adsorption of Ba^{++} ion or simply due to the adsorption of the anion. In a previous paper (Mukherjee and Chaudhuri, J. Chem. Soc., 1924, Vol. 125, p. 795) reasons have been given which indicate that acetate and benzoate ions are more strongly adsorbed than Cl^- ion. This observation is in agreement with the observed influence of sodiumacetate and sodium benzoate on NaCl . The anion adsorption in these cases is therefore clearly established.

Regarding the effect of LiCl on BaCl_2 Weiser has attributed it to the displacement of Ba^{++} ion by Li^+ ion as he has actually observed that the precipitate carries with it

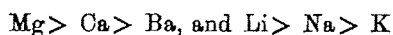
* The result for the pair LiCl and BaCl_2 are taken from Freundlich's *Kapillär-chemie*, p. 634 (1922).

less Ba in the presence of LiCl than in its absence. It is however necessary to point out that this observation in itself does not justify Weiser's conclusion. Apart from the difficulties of interpreting analytical data on adsorption (cp. W. O. Ostwald *Koll-Z.* 30 (1919), 279), Weiser's observation only shows that a smaller number of barium ions are present in the "double layer." It does not follow that there is also a smaller number of barium ions fixed on the surface than in the other case. The distinction between the adsorbed ions which are free to move under an impressed electrical field and those which are not free to move has been overlooked. The relative ratio of the two cations per unit surface in the fixed layer of ions which really determine the diminution in the electrical charge is not necessarily identical with that in the freely moving second sheet of the Helmholtz double layer. Analytical data cannot evidently give an idea of the distribution in either layer. It gives the idea of the total effect due to both layers assuming that the adsorption of the solvent is negligible. Weiser's interpretation will be true if coagulation takes place when the particles are practically neutral as in that case there will be no freely moving ions and all the cations are fixed on the surface. There is no justification for such an assumption.

We would now point out that in all these cases the assumption of a small adsorption of an anion will be sufficient to explain the observed effects* without recourse being had either to considerations of hydration or to displacement of adsorption. If we consider the experiments of Ellis, Powis and Kruyt at low concentrations of the electrolyte we find that there is in most cases a slight rise in the negative charge when the electrolyte is KCl or LiCl. We see that in the case of a chloride with a cation

* Of course we cannot say that this is actually the case in the absence of relevant data on the electrical charge.

of low coagulating power the increase in the charge may be more pronounced (cp. the curves given by Freundlich *Kapillarchemie*,* page 354, 2nd edition). In that case there ought to be a gradation in the effects of electrolytes having common anion and cations of same valency but different coagulating power. The coagulating power of lithium is the weakest among the alkali metal ions and that of magnesium among the divalent cations Ba, Sr, Ca, Mg, etc. Both Freundlich and Weiser have observed that lithium and magnesium show the most pronounced effect. Our experiments also support this observation as will appear from the data given above. Where the anions are adsorbed to a marked extent the greater increase in the negative charge is reflected in a greater difference in the coagulating concentrations of different cations of the same valency. We notice that the influence of sodium benzoate is in the order



that is the reverse order of their precipitating power. If we now contrast the effect of mixing sodium chloride instead of sodium acetate or sodium benzoate we find that the individual variations between barium chloride, calcium bromide and magnesium chloride are scarcely perceptible. If the displacement of adsorption of these cations varied from one to another one would then have expected a greater difference between them. Magnesium in no way shows characteristic difference compared to barium or calcium. The anion adsorption in the case of

* If similarly in the case of arsenious sulphide there is an increase in the charge at low concentration of these chlorides then it is not necessary to assume either hydration or the displacement of adsorption. In collaboration with Mr. S. G. Chaudhuri measurements are being made on the variation in the rate of cataphoresis of Arsenious sulphide particles with the change in concentration of acids. So far HCl and H_2SO_4 have been studied. The variation in charge is very complicated and depends probably on whether we are dealing with an orange or yellow sol. on the concentration of H_2S and probably on the reaction between H ion and the stabilising ion adsorbed on the surface of the colloid.

the chlorides is less pronounced because we are dealing with a relatively less adsorbable anion and cations with fairly strong coagulating power. Our contention is that it is the initial rise in charge at low electrolyte concentration which is to a large extent responsible for all these effects. It does not matter whether the increase in charge is due to a strong adsorption of the anion or to a weak adsorption of the cation as in the case of sodium benzoate and lithium chloride respectively. Recognising that on the addition of a small quantity of an electrolyte (say up to 66% of its coagulating concentration) there is an increase in the charge, the protecting effect of such an increase will of course be more prominent if the coagulating cation has a weaker precipitating power. That is why we find so great an effect of lithium chloride on magnesium chloride or of sodium benzoate or sodium acetate on magnesium chloride. The effect of sodium acetate on calcium bromide is not in any way less pronounced than that of lithium chloride on magnesium chloride and the effect of sodium benzoate on lithium chloride is fairly comparable to that of lithium chloride on magnesium chloride.

Similarly potassium trichloracetate has a greater effect than the acid on the coagulating concentration of the barium salt in keeping with the lower coagulating power of the potassium ion compared to that of the hydrogen ion. The pair barium benzoate and barium chloride show a marked contrast to sodium benzoate and sodium chloride. The total barium ion concentration remains fairly constant. Whereas in the case of sodium acetate and sodium chloride the total sodium ion concentration becomes more than double the coagulating concentration of sodium ions when only sodium chloride is used. The difference is probably due to the low anion concentration of the barium salts and the greater coagulating power of

the barium ion. There ought to be from our point of view no increase of charge at low concentration of barium salts. The curves of Ellis and Powis show this peculiarity. Potassium ferrocyanide and potassium chloride on the other hand show a weaker effect than sodium acetate and sodium chloride. This is probably due to the greater coagulating power of potassium ion on the one hand and the weaker adsorption of $\text{Fe}(\text{CN})_6$ ion on the other hand in spite of its higher valency as shewn in a previous paper.

We would again repeat that in order to clearly understand the nature of these effects the corresponding measurements of the charge is absolutely necessary and discussion on the displacement of adsorption might be profitably postponed till we have obtained the necessary data.

Lastly we would make a few observations on ionic antagonism as observed in nature. It is rather rash to draw conclusions from a few experiments on coagulation in the laboratory and to conclude from the similarity of effects that there is a similarity in the cause. At the same time we might suggest that at least one of the main causes which is responsible for ionic antagonism as observed by Lillie, Osterhout, Loeb and Clowes (J. Phys. Chem., 20, 1916) is the effect of the ions on the electrical charge of the dispersed system. The similarity in the effects is probably to be attributed to this common factor. Clowes states "whatever the ultimate theoretical interpretation may be the close correspondence between data accumulated in such widely diversified fields affords substantial evidence of the existence of some heretofore unappreciated fundamental physical principle" and this fundamental physical factor might be the electrical charge.

[Received, Nov. 10, 1924.]

Chemical Knowledge of the Hindus of Old.¹

BY

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An eminent Belgian Indologist, Goblet d'Alviella, has very justly observed that India is a land of paradoxes, that whatever is of ancient origin excites our admiration—her literature including her unrivalled dramas, her transcendental philosophy of the *Upanishads* and the *Geeta* attracted the attention of the West long ago. India was once the cradle of mathematical sciences including arithmetic and algebra; the system of notation, popularly ascribed to the Arabs, is really the product of the Hindu brain.

Max Müller says somewhere that if India had presented no other gift to Europe than that of the numerals, the debt of the latter to the former would have been unrequitable.² Ancient Assyria, Babylon and

¹ Inaugural address delivered by the President, Indian Chemical Society, at its first annual General Meeting held at the chemistry lecture theatre, Hindu University, Benares.

² The learned Professor of Sanskrit of Oxford University says "In science too, the debt of Europe to India has been considerable. There is, in the first place, the great fact that the Indians invented the numerical figures, used all over the world. The influence which the decimal system of reckoning dependent on those figures has had not only on mathematics, but on the progress of civilisation in general, can hardly be overestimated. During the 8th and 9th centuries the Indians became the teachers in arithmetic and algebra of the Arabs and through them of the nations of the West. Thus, though we call the latter science by an Arabic name, it is a gift we owe to India."—Macdonnell's *History of Sanskrit Literature*, p. 424.

Egypt exist only in their monuments, cuneiform inscriptions or hieroglyphs, inscribed on slabs of stone or baked clay. The recent discoveries in Tutankhamen mausoleum have yielded many new specimens of Egyptian art of all kinds. Rome and Greece live in their literature and philosophy, but the Hindu nation persists to-day as she did 2,500 years ago, when Gautama Buddha preached at Benares, the sacred city where we are holding our meeting to-day. Sakya Muni knew that if he could make a breach in the citadel of Hindu religion and culture, the whole of India would readily embrace his new doctrine. For a time Brahminical supremacy must have been shaken to its foundation as is proved by the archæological findings of Sarnath now some five miles from this city. But the tenacious vitality of the Hindu religion is something marvellous and it struck sagacious tourists and observers like Pierre Loti. Even to-day European visitors who find the pious Hindu performing his daily religious practices and ablutions at the bathing ghats of the Ganges can have but little difficulty in coming to the conclusion that impact with the West has scarcely produced any effect on the Hindu. He pursues his daily even tenor of life as his ancestors did twenty-five centuries ago. No wonder that the poet should exclaim :—

“ The East bowed low before the blast
In patient, deep disdain,
She let the legions thunder past
And plunged in thought again.”

No doubt the Hindus have been meditating—ever lost in abstruse metaphysical subtleties, but, all the same, in ancient India physical science found her votaries. I have barely time to allude to the atomic theory as propounded

in the Vaiseshika System of Kanāda, which anticipates the doctrine of Anaxagoras, Empedocles, etc. I shall limit myself this afternoon to the keen powers of observation as also the necessity of experimental methods enjoined by the Hindus of old, so far as chemical processes are concerned. Indeed, Dhundukanātha, the author of the standard iatro-chemical treatise *Rasendra Chintamani*, (lit. gems of mineral preparations), says—"They are alone to be regarded as real teachers who can show by experiment what they teach. They are the deserving pupils, who, having learnt the experiments from their teachers can actually perform them. The rest, both the teachers and the pupils, are merely stage-actors."¹

This author, again, acknowledges his indebtedness to the standard work on the subject, *Rasārṇava*, in which occurs an elaborate account of the processes of sublimation, distillation, etc., as also of the apparatus required for the process. Indian alchemists are also eloquent in their veneration for and indebtedness to the great adept, Nagārjuna, to whom is ascribed the invention of the above processes. One instance will suffice to give you an idea of the methods adopted for the purification of mercury.

मिश्रितौ चेद्भस्मे मागवज्ज्वलौ विक्रयहेतुना ।

ताभ्यां स्यात् कृत्रिमो दोषः तस्मात्तिः पातनद्वयात् ।

¹ अशीषं बहुविद्भ्यां सुखावपश्यं

शास्त्रेषु स्थितमकृतं न तद्विद्वामि ।

यत् कर्म व्यरचयमयतो गुरुना

प्रीदानां तदिह वदामि वीतशङ्कः ॥

अध्यापयन्ति यदि दृश्यन्ति कसले

स्तेन्य कर्मगुरवो गुरुवत् एव ।

शिष्यास्त एव वदन्ति गुरोः पुरो ये

श्रेयाः पुनस्तद्वदन्ति न भवन्ति ॥

The above, literally rendered, runs as follows:—
 “Fraudulent dealers adulterate (alloy) mercury with lead and tin, hence these impurities are to be removed by subjecting the mercury to triple distillation.”

The identification of metals by the colouration of their flames is referred to in *Rasārṇava*—

“Copper yields a blue flame, that of the tin is pigeon-coloured, that of the lead is pale tinted¹..... ”

We are not aware of similar tests being applied anywhere at such an early period as a qualitative test for metals.² As regards the high degree of skill in metallurgy attained by the Hindus, it is enough to mention the iron pillar near Delhi.³ In the ancient Hindu literature only six metals are mentioned, *viz.*, gold, silver, iron, lead, tin and copper. The name of a seventh metal—zinc—occurs in European history for the first time in the works of Paracelsus, who leaves us in the dark as to the nature of his “zincken,” which he designates as “semi” or bastard metal.

Libavius was the first to mention the properties of zinc more exactly although he was not aware that the

¹ Cf. “Lead compounds impart a pale tint to the non-luminous gas flame.”—Roscoe and Schorlemmer's *Chemistry*, Ed. 1879.

² Cardan (1501-1576) is perhaps the earliest to notice that the colour of the flame varies with different metals—Hoefer's *Hist. d. Chim.* Vol., II, p. 95. Ed. 1869.

³ Taking A.D. 400 as a mean date—and it certainly is not far from the truth—it opens our eyes to an unsuspected state of affairs to find the Hindus at the age capable of forging a bar of iron larger than any that had been forged even in Europe up to a very late date. As we find them, however, a few centuries afterwards using bars as long as this *lat* in roofing the porch of the temple at Kanaruc, we must now believe that they were much more familiar with the use of this metal than they afterwards became. It is almost equally startling to find that, after exposure to wind and rain for fourteen centuries, it is unruined, and the capital and inscription are as clear and as sharp now as when put up fourteen centuries ago.”

“There is no mistake about the pillar being of pure iron. General Cunningham had a bit analysed in India by Dr. Murray and another portion was analysed in the School of Mines here by Dr. Percy. Both found it pure malleable iron without any alloy.”—Fergusson's “*History of Indian and Eastern Architecture*, Ed. 1899, p. 508.

Even now forged masses of such size are exceptional.

metal was derived from the ore known as 'calamine.' He states that "a peculiar kind of tin is found in the East Indies, called 'calaëm.' Some of this was brought to Holland, evidently by the Dutch East India Company, and came into his hands." The extraction of zinc from the ore (calamine) can be followed in every detail from the account left to us in *Rasārnava* and specially *Rasaratnasamuchchaya*. The process as given in the latter work is reproduced below. The literal rendering of it runs thus :

"Rub calamine with turmeric, the chebulic myrabolans, resin, the salts, soot, borax¹..... Fill the inside of a crucible with the above mixture and dry it in the sun. Close its mouth with a perforated saucer. A vessel filled with water is embedded in the ground, over which the above vessel charged with the mixture is inverted, which is again heated as shown in the figure, by means of a charcoal fire. The operation is stopped when the *flame issuing from the mass changes from blue to white*. The essence of the metal, which drops into the water and has the lustre of tin, is to be collected." Indeed, the process, so elaborately given above, might be quoted almost *verbatim* in any treatise on modern chemistry.² It is practically the same as *distillatio per descensum*—the flame of a bluish tint issuing from the mouth of the crucible indicates the combustion of carbon monoxide so often observed in metallurgical operations.

¹ It is scarcely necessary to point out that highly carbonaceous substances like resin, turmeric, etc., being heated in the absence of air yield carbon in a fine state of division.

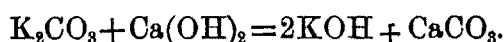
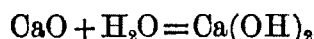
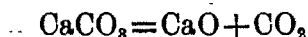
² *Of*. "A mixture of two parts of ground roasted ore and one part of coal-dust is brought into the retorts, each holding about 40 pounds of the mixture. As soon as the temperature has risen high enough, the reduction begins and carbon monoxide is evolved and burns from the end of the clay adapter with a blue flame." (The italics are ours)—Roscoe and Schorlemmer's Chemistry, Ed. 1879, Vol. II, Part I, p. 225.

It is not, of course, claimed that the ancient Hindus knew that the blue colour was due to the combustion of carbon monoxide, but what I should like to lay particular stress upon is the power of keen observation underlying the description.

The ancient Hindus knew the distinction between potassium carbonate and sodium carbonate—the former is called *yavakshāra* (lit. ash from the spikes of barley), and the latter *sarjikakshāra*, (equivalent to *natron* from Egypt). The earliest record of this is to be found in the old Hindu work, the *Susruta*. The *Charaka* and the *Susruta* are the two standard and authoritative treatises on *Ayurveda* (lit. science of life). The *Charaka* is more concerned with medicine, while the *Susruta* relates more or less to surgery. Here we have a drop of 2,000 years from the *Susruta* to the remarkable discoveries of Joseph Black. In the *Susruta* the two modifications of alkali are referred to as *tikshnakshāra* (*tikshna*, i.e., sharp or caustic; *kshāra*, i.e., alkali), and *mridukshāra* (i.e., mild alkali). The distinction between the two is quite clear. In the days of my boyhood the ashes of the plantain tree (*Musa sapientum*) were used by washermen for cleaning clothes. The reason is that it is very rich in potassium carbonate. In the *Susruta* we have many land plants mentioned which have been botanically classified in Uday Chand Dutt's *Materia Medica of the Hindus*. The *Susruta* says "on an auspicious day cut the plant down, burn it and boil the ashes with water in an iron pan and then filter through cloth folded several times." This, says the *Susruta*, is *mridukshāra*. You know what actually takes place in this process. The clean solution that is obtained is rich in potassium carbonate and is termed mild alkali.

Next comes the description of the preparation of caustic alkali, and this is the most scientific portion.

“Collect several kinds of limestone and shells and burn them strongly and add water to the resulting product. Next mix this slaked lime with the lixiviated liquid obtained above and boil and stir with an iron ladle.” The reactions that take place here can be represented in the modern way by the following equations:



This method, you will look for in vain in any European treatise before the 16th or the 17th century. The process as given in the *Susruta* is so scientific that it can be bodily transferred to any modern text-book on chemistry. Besides recommending the use of an iron vessel for boiling the liquid, the book further says that the *kshāra* so obtained, must be stored in an iron vessel with its mouth closed :

आयसे कुम्भे संवत्समुद्धे निदध्यात् ।

The *Susruta* cannot, of course, be credited with having known that carbon dioxide was to be excluded from the vessel to prevent the caustic solution from being acted upon. But the physicians of those days must have certainly realised by empirical methods that the causticity would be diminished if these precautions are not taken. Even to-day we keep caustic potash, either in iron or silver vessels. The points to be noted here are that the *Susruta* gives not only a very accurate method of preparation and preservation of the two kinds of alkali but also the distinction between the two varieties, *tikshnakshāra* and *mridukshāra*, is clearly

recognised. Davy isolated potassium and he says, "The ancients did not know how to distinguish between potassium carbonate and sodium carbonate." But in our *Ayurveda* this sharp distinction has been clearly stated.

Between the *Susruta* and Joseph Black lies a gap of some 2,000 years. Black was an M.D. of Edinburgh. In his Doctorate thesis (presented in 1755) he gave for the first time the scientific explanation of the difference between caustic and mild alkalis. He heated magnesium carbonate using the balance at each stage of the experiment, and pointed out that on strong heating there was a loss in weight. He also pointed out that a gas was given out which was called "fixed air." Ramsay in his *Life of Black* says "Quicklime is formed by heating lime-stone in the fire; it thereby acquires its burning properties or causticity." Black's essay was an epoch-making one.

M. Berthelot, under whose inspiration I took to writing my *History of Hindu Chemistry*, in reviewing my book says of this portion "that the Hindus possibly got their knowledge of this method from the Portuguese." (*Journal des Savants*, Jan. 1903, p. 34.) But against that I may point out that Chakrapāni, who was the court physician of Nayapāla (1050 A.D.), King of Gour, in the treatise which goes by his name, quotes this mode of preparation verbatim from the *Susruta*. A much older treatise, the *Vagbhata* also does the same. In the course of my studies, I came across a remarkable passage in a Buddhist work which dates as far back as 140 B.C.,—I mean the *Milinda Panho*. Professor Rhys Davids translates the portion as follows: "And when the inflammation had gone down and the wound had become sweet, suppose he were then to cut into it with a lancet, and burn it with caustic. And when he had

cauterized it, suppose he were to prescribe an alkaline wash..... Now tell me, O King! would it be out of cruelty that the surgeon..... thus cut with the lancet and cauterized with the stick of caustic."¹

It must be admitted on the other hand that the discovery of Black was quite independent and he showed that the difference between the mild and the caustic alkalis was due to the presence of carbon dioxide in the former. The *Susruta*, of course, does not say anything of this kind.

The use of metallic preparations mentioned in the Hindu Pharmacopœia also dates from a very early period. In Europe Paracelsus was, as we have said, the first to introduce metallic preparations into medicine. But in India, Vrindā who preceded Chakrapāni by at least a century and therefore must have flourished about the 9th Century A.D., or even earlier, was the first to prescribe 'Kajjvali' (black sulphide of mercury) as a medicine. Chakrapāni gives an elaborate description of the process of making 'Kajjvali'. In Europe this preparation was not known before the 17th century.²

I need not proceed further. The knowledge of pharmacy which the Arabs brought to Europe was derived from the Hindus. *Ex oriente lux*. I shall conclude with the apposite words of that illustrious French Chemist, Jean Baptiste André Dumas: "What an awakening for Europe! After two thousand years she found herself again in the position to which she had been raised by the profound intellect of India and the

¹ *Sacred Books of the East*—Vol. XXXV, p. 168.

² Das Schwarze Schwefelquecksilber lehrte zuerst Turquet de Mayerne, im Anfange des 17 Jahrhunderts, durch Zusammenreiben von warmen Quecksilber mit geschmolzenem Schwefel darstellen"—Kopp: *Gesch. d. Chem.* Vol. IV, 186.

acute genius of Greece." (The first *Faraday Lecture* delivered before the Chemical Society, June 17, 1869).¹

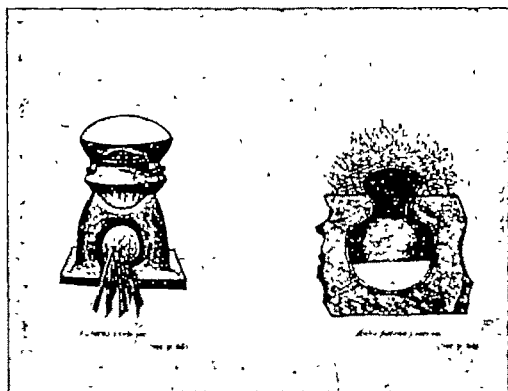
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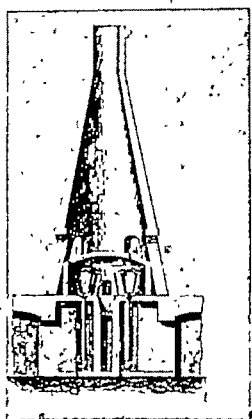
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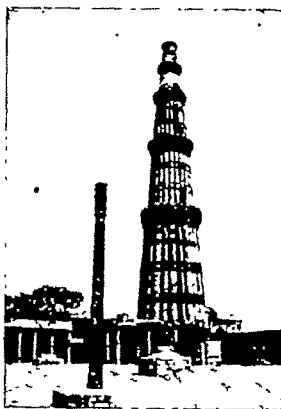
¹ Hofer in his admirable *Histoire de la Chimie* also expresses the same view "L'Inde est le berceau de la filiation des peuples qui marchent à la tête de la civilisation."—Vol., I, Ed. 1866.



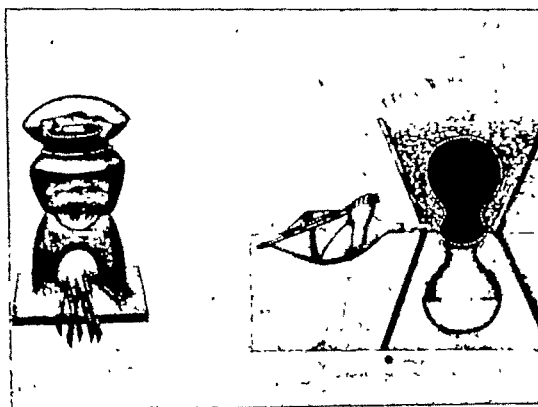
Apparatus for sublimation and
distillatio per descensum.



A modern method of
extraction of zinc.

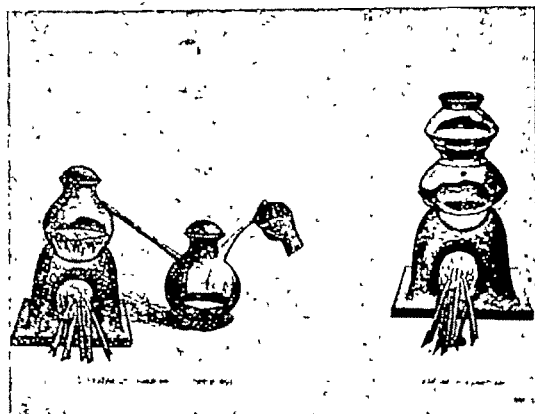


The iron pillar and the
Kutab minar near Delhi.



Fumigating
apparatus

Extraction of zinc
from calamine.



Apparatus for
distillation

Apparatus for extraction
of mercury from cinnabar

New Mercury-ammonia Compounds.

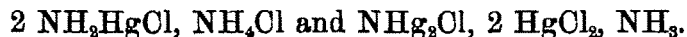
BY

PRIYADARANJAN RÂY

AND

PARES CHANDRA BANDOPADHYAY.

The action of ammonia upon various simple and some double or complex mercury-salts like potassium mercuric iodide and sodium mercuric nitrite, etc., has been studied by various investigators from a very early time. A very large number of complex mercury-ammonia compounds have been described. But the subject is still far from being exhausted. The present paper deals with the preparation and properties of some new ammoniacal compounds of mercury and with the description of some interesting reactions. By the action of ammonia and ammonium carbonate upon mercuric chlor-iodide under different conditions, the following compounds have been obtained :



Mercuric brom-iodide, on the other hand, gave only more or less pure dimercurammonium bromide. By the action of potassium thiocyanate upon infusible white precipitate a new mercury-ammonium thiocyanate of the formula NHg_3SCN has been obtained. Action of potassium chromate upon infusible white precipitate, on the other hand, gave rise to the formation of a chromate of Millon's

base. Potassium bromide gave dimercur-ammonium bromide and potassium iodide gave the iodide of Millon's base. An arsenate of Millon's base which has not been described in the literature has been obtained by the action of ammonia upon mercuric arsenate.

EXPERIMENTAL.

Action of Ammonia upon Mercuric Chlor-iodide.—

A solution of mercuric chlor-iodide was prepared by saturating mercuric chloride solution with mercuric iodide. The solution was then added drop by drop with constant stirring to a large excess of strong ammonia. An orange-yellow precipitate was formed, it was filtered and washed first with ammonia, then with water and finally with alcohol. The substance was then dried in vacuum over sulphuric acid.

The substance was soluble in hydrochloric acid but not in sulphuric acid and gave ammonia with caustic soda. On heating in a dry test tube, ammonia was given off and a sublimate consisting of mercurous chloride, mercuric iodide, ammonium chloride and some metallic mercury was formed. Several samples were prepared under varying conditions of temperature and concentration of the chlor-iodide solution and gave the same composition. The same compound was also obtained from an excess of boiling ammonia solution.

Analysis:

Found: Hg=85.7, 85.86, 85.1, 85.1, 85.4 per cent.

Cl =6.37, 6.37, 6.3, 6.34 per cent.

I =4.01, 3.91 per cent.

N =3.26, 3.17 per cent.

$6\text{NHg}_2\text{Cl}$, NHg_2I , $2\text{H}_2\text{O}$ requires Hg=85.52,

Cl =6.5, I=3.9, N=3.01 per cent.

It may also be represented as a triple compound of dimercur-ammonium chloride, chloride of Millon's base and iodide of Millon's base.

It should, however, be pointed out that only infusible white precipitate is obtained by the addition of mercuric chloride to a large excess of ammonia.

Secondly, a white precipitate was formed by adding dilute ammonia to an excess of the chlor-iodide solution; addition of ammonia must be stopped before the precipitate showed any yellow tinge; hence the mercury salt should always be in large excess. The substance thus prepared contained no iodine. The precipitate was washed with alcohol and dried in vacuum over sulphuric acid.

It was soluble in acids, gave ammonia with caustic soda or ammonium bromide. Dry ignition decomposed it into ammonia, mercurous chloride and water.

Analysis :

Found: $\text{Hg} = 78.7, 79.02$ per cent.

$\text{Cl} = 16.23, 16.17$ per cent. $\text{N} = 3.46$ per cent.

$4\text{NH}_2\text{HgCl}, \text{NH}_2\text{HgCl}, 2\text{HgCl}_2$ requires $\text{Hg} = 80$; $\text{Cl} = 16.1$ and $\text{N} = 3.5$ per cent.

Action of Ammonium Carbonate upon Mercuric Chlor-iodide.

To an excess of pure ammonium carbonate solution, a solution of mercuric chlor-iodide was added drop by drop. The precipitate first formed soon redissolved; with the addition of more mercuric salt a permanent white precipitate was formed. It was washed first with dilute ammonium carbonate solution, then with alcohol and dried in vacuum over sulphuric acid. The substance tended to decompose on treatment with water turning

yellow. On heating in a dry test tube, the substance first turned yellow, partly fused and then decomposed with evolution of ammonia and gave a white sublimate of Hg_2Cl_2 . It was soluble in acids, gave off ammonia with caustic soda and ammonium bromide.

Analysis:

Found: $\text{Hg} = 71.4, 71.7$; $\text{Cl} = 19.52, 19.41$.

$\text{N} = 7.504$.

NH_2HgCl , HgCl_2 , 2NH_3 requires $\text{Hg} = 71.9$; $\text{Cl} = 19.1$ and $\text{N} = 7.5$ per cent.

The substance appears to be a double compound of one molecule of infusible white precipitate and one molecule of fusible white precipitate. The presence of the latter was indicated by its ready decomposition on warming with water with the development of a yellow tinge and the passage of ammonium chloride in the filtrate.

On the other hand, when ammonium carbonate solution was added to an excess of the mercuric salt, a white precipitate was obtained. It was filtered, mother liquor drained off by strong suction, washed with alcohol and then dried in vacuum over sulphuric acid.

The substance was soluble in acids, on heating in a dry test tube it decomposed with evolution of ammonia and gave a white sublimate of mercurous chloride.

Analysis:

Found: $\text{Hg} = 78.6, 78.9, 78.45$; $\text{Cl} = 17.5, 17.6$,

17.6 ; $\text{N} = 2.9, 2.6, 2.6$.

NHg_2Cl , 2HgCl_2 , NH_3 requires $\text{Hg} = 79.3$; $\text{Cl} = 17.6$,

$\text{N} = 2.77$ per cent.

It should however be mentioned here that by the action of ammonium carbonate solution upon mercuric chloride solution alone, infusible precipitate is always obtained, which is again soluble in an excess of ammonium carbonate solution.

As these compounds were all insoluble in water, nitric and sulphuric acids and incompletely decomposed by alkali and as some of them contained both chlorine and iodine, some difficulties arose as regards their analysis which were overcome in the following way:—

Mercury was estimated as mercuric sulphide after dissolving the substance in hydrochloric acid. Estimation of chlorine was made by mixing the substance with six times its weight of anhydrous sodium carbonate in a porcelain crucible and heating the latter slowly with the lid in position on an asbestos ring—Mercury escaped by vaporisation and chlorine remained fixed as sodium chloride. If iodine were present, a part of it vaporised as mercuric iodide and a part was fixed as sodium iodide. After expelling all the mercury, the mass was acidified with nitric acid, treated with ammoniacal silver nitrate solution, any iodine present being precipitated, the solution was filtered, acidified with nitric acid, silver chloride was reprecipitated and weighed as AgCl. Iodine was estimated as follows:—the substance was dissolved in cold hydrochloric acid and the mercury was precipitated as mercury sulphide and then the filtrate was rendered alkaline with sodium carbonate and evaporated to dryness. The mass was then treated with ferric alum and sulphuric acid, iodine was distilled, absorbed in potassium iodide solution and then titrated with standard sodium thiosulphate solution. Nitrogen was estimated by Duma's method.

Action of Ammonia upon Mercuric Brom-iodide.—

In the first place a solution of mercuric brom-iodide prepared by saturating a solution of mercuric bromide with mercuric iodide was added drop by drop to an excess of ammonia. The solution first turned yellow, then reddish brown and with the addition of more mercuric salt a reddish brown precipitate was formed. The precipitate was washed with ammonia water and then with alcohol and dried in vacuo over strong sulphuric acid.

The substance was soluble in hydrochloric acid; when heated in a dry test tube it decomposed into mercuric iodide, mercurous bromide and some metallic mercury but gave no ammonia.

Analysis of different samples showed variable composition; the substance seemed to be a mixture of NHg_2Br with a little NHg_2I .

On the other hand, when ammonia was added to an excess of the mercuric brom-iodide solution, a yellow precipitate was formed. On examination it was found to be almost identical with NHg_2Br usually obtained by the action of ammonia upon boiling mercuric bromide solution. The same compound NHg_2Br was also obtained when ammonium carbonate solution was added to an excess of mercuric brom-iodide solution. This compound was soluble in an excess of ammonium carbonate solution.

Action of some Potassium Salts upon Infusible White Precipitate.—

It has been shown (Gazzetta, 1893, 22, 11,557) that when the mercuri-ammonium salts are heated with solution of potassium or sodium salts, they are decomposed with the evolution of ammonia and formation of mercuric salts (Kane, Ann. Chim, Phys.; Rammelsberg,

Poggendorf's Annal. Phys. Chem., 48, 182). We studied this reaction again and found that by the action of potassium salts, an intermediate compound was first formed. In most cases this compound was very stable and went into solution when boiled with a large excess of the reagent.

Action of Potassium Sulphocyanide Solution upon Infusible White Precipitate and the Formation of Dehydrated Sulphocyanide of Millon's Base.—

A freshly prepared white precipitate was treated with a strong solution of potassium sulphocyanide, first in the cold and then heated on the water-bath for about three hours with constant stirring. A large amount of ammonia was evolved and the residue turned yellow. It was filtered, washed with water and dried in vacuum over sulphuric acid.

The substance was soluble in large excess of potassium sulphocyanide after boiling for some time and evolved a large amount of ammonia. It was also soluble in acids. On heating in a dry test tube it exploded forming a black deposit of mercuric sulphide, a mirror of metallic mercury and gave out a garlic smell.

Analysis :

Found: $\text{Hg}=84.6, 84.6$; $\text{S}=6.7, 6.78$;

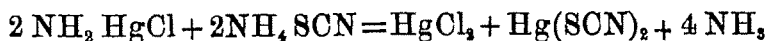
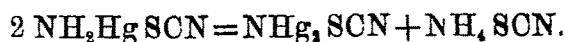
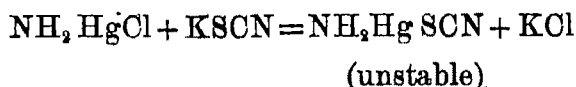
$\text{N}=6.28, 6.24$ per cent.

NHg_2SCN requires $\text{Hg}=84.8$; $\text{S}=6.76$ and

$\text{N}=6$ per cent.

The filtrate after the separation of the yellow product was found to contain free ammonia and ONS' , Cl' , CN' , K^+ and Hg^{++} ions. On allowing the solution to crystallise after evaporation the double salt $\text{Hg}(\text{SCN})_2 \cdot \text{KSCN}$ mixed with some $\text{Hg}(\text{SCN})_2 \cdot \text{NH}_4\text{SCN}$ were obtained.

The reaction that occurs may be represented as follows:—



This compound has not been described by any previous worker and corresponds to the analogous compounds NHg_2Cl , NHg_2Br etc.

Action of Potassium Chromate upon Infusible White Precipitate and the Formation of Chromate of Millon's Base.—

Freshly prepared white precipitate was treated with a strong solution of potassium chromate on the water-bath or about 12 hours with constant stirring; ammonia was evolved and a greenish yellow product was obtained. It was then filtered, washed and dried in vacuo over sulphuric acid.

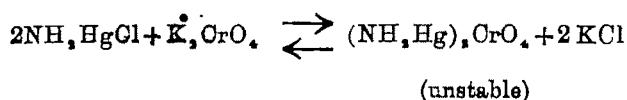
On heating in a dry test tube the substance decomposed into mercurous and mercuric chromate and water but gave no ammonia.

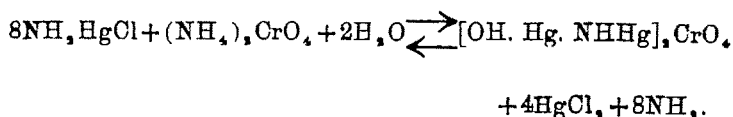
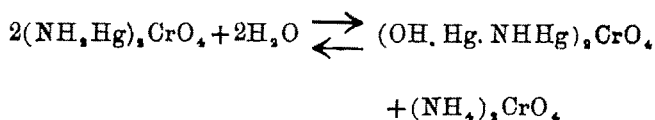
Analysis :

Found: $\text{Hg} = 81.3, 82.3$; $\text{Cr} = 5.7, 5.3$;

$\left[\text{O} < \begin{smallmatrix} \text{Hg} \\ \text{Hg} \end{smallmatrix} > \text{NH}_2 \right]_2 \text{CrO}_4$ requires $\text{Hg} = 81.7$; and $\text{Cr} = 5.3$ per cent.

The reaction that occurs may be represented as follows:—





The same compound has been described by Hensgen who obtained it by dissolving mercuric oxide in ammonium bichromate and then heating the solution with excess of ammonia. (Hensgen, Rec. Trav. Chem., 1887, 5, 187.)

The infusible white precipitate when treated in a similar way with potassium bromide solution avoiding a large excess, a yellow product soluble in excess of potassium bromide solution was obtained. This was found to be identical with NHg_2Br .

Similarly the first action of potassium iodide solution upon infusible white precipitate was found to cause the production of iodide of Millon's base which dissolved in an excess of potassium iodide solution evolving a large amount of ammonia.

Potassium arsenite, on the other hand, reduced the infusible white precipitate and metallic mercury was separated. No perceptible reaction was observed in the cases of sulphate, phosphate, fluoride, borate and arseniate of potassium.

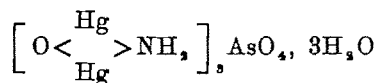
Preparation of Arseniate of Millon's Base.

No arsenical mercury ammonium compound has been described by any worker. A compound which may be regarded as an arseniate of Millon's base was prepared in the following manner. Freshly prepared mercuric arseniate was digested with ammonia when the yellow mercuric arseniate turned white. It was then filtered,

washed with dilute ammonia, then with alcohol and dried in vacuum over sulphuric acid. A slightly yellowish product was obtained after drying.

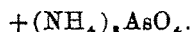
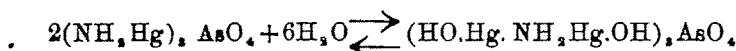
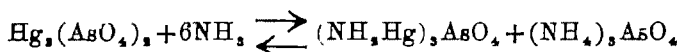
Analysis:

Found : Hg=79.3, 79.7 ; As=5.27 ; N=3.09.



requires Hg=80.5 ; As=5.0 ; N=2.84 per cent.

The reaction occurs as follows :—



Action of Sulphur Dioxide upon Infusible White Precipitate.—

When sulphur dioxide gas was passed into water in which freshly prepared infusible white precipitate was suspended, the latter went into solution which on evaporation gave a crystalline substance of the composition HgSO_3 , NH_4Cl .



HgSO_3 formed dissolved in NH_4Cl giving the double salt.

The same compound has also been described by Ruff and co-workers (Zeit. Anorg. Chem., 1920, 114, 203). But the mechanism of the action represented by the authors of the above paper is rather unusual and has no strong

NADIA CHEMICAL WORKS,

41, SHRI NARAYAN DAS LANE,
CALCUTTA.

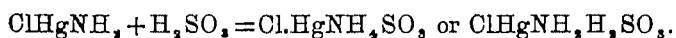
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evidence in support of it. It was represented as follows:—



This is a rather far-fetched representation of the case.

It is however a known fact that insoluble mercuric salts easily dissolve in ammonium salt solutions and form double salts.

Action of Nitrous Acid upon Infusible White Precipitate.—

When N_2O_5 is passed into cold water containing freshly prepared infusible white precipitate in suspension, the latter dissolved and the solution on evaporation under reduced pressure gave double salt of mercuric chloride with ammonium nitrite mixed with a little nitrate. The substance was never obtained pure as ammonium nitrite in solution began to decompose on concentrating the solution.

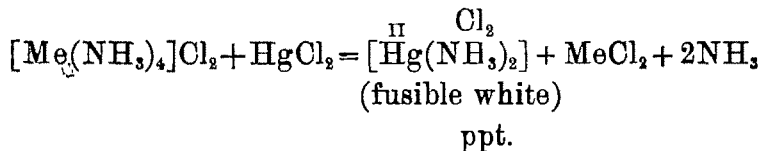
Action of Mercuric Chloride upon Zinc or Cadmium Ammonium Chloride.—

Zinc or cadmium ammonium chloride solution was prepared by saturating an ammonium chloride solution with the hydroxides of the metals. To this solution a solution of mercuric chloride was added. A white crystalline precipitate was obtained.

The precipitate on heating in a dry test tube, fused and decomposed with the evolution of a large amount of ammonia forming a white sublimate of calomel. No zinc or cadmium was found in the product. It turned yellow with water. That is, it behaved in every respect like fusible white precipitate.

An analysis of the product confirmed this view and the substance was found to be identical with the fusible white precipitate. Action of ammonia upon mercuric chloride solution alone gives however under all circumstances only the infusible white precipitate.

The reaction can be represented as follows :—



where Me = Zn or Cd.

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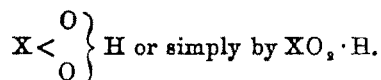
Thermo-chemical Investigations on the Constitution of Acids in Solution.

BY

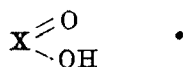
D. D. KARVE.

It is well known that the properties of acids are generally explained by the presence of H-ions, and the strength of acids depends on the concentration of these ions. The undissociated acids possess, according to the classical theory, no activity. Some recent theories however postulate that concentrated acids, or even pure acids, are fully dissociated. Hantzsch¹ has studied the behaviour of undissociated acids and has advanced his extended theory of pseudo-acids, which can be summarised as follows :

1. The properties common to all acids (*e.g.*, action on indicators, on diazoacetic ester, on cane sugar, etc.) are not peculiar to the H-ions but are due to the presence of an ionogen H-atom (*i.e.*, an H-atom which has given up one electron to the oxygen of the acid radical). The H-atom is however not bound up with any single O-atom, but is loosely connected with as many O-atoms as possible. These are the so-called true acids and are represented graphically by

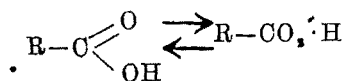


2. In the second class of acids the H-atom is bound down to one O-atom of the acid radical forming a hydroxyl group. These are the pseudo-acids which are represented graphically as



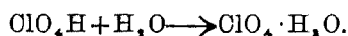
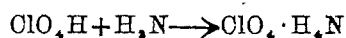
¹ Ber., (1917), 50, 1422; Z. Elektrochem., (1923) 29, 221; (1924) 30, 194

3. The third class of acids are the equilibrium acids, the typical representatives of this class being acetic and formic acids. Both the forms are here in dynamic equilibrium represented by



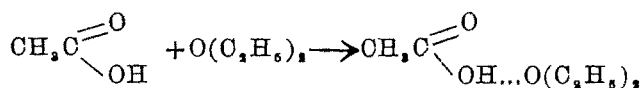
and this is affected by the particular solvent in which they are dissolved and by the concentration of the acid in it. Certain solvents like water move the equilibrium point to the right, while certain others like ether shift it towards the left.

4. The true acids form oxonium salts with water in the same way as they form ammonium salts with ammonia :

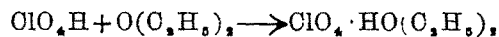


Water however being a very weak base, these salts are practically completely dissociated into their components even in moderately dilute solutions.

5. With ether and similar compounds the pseudo-acids form pseudo-salts or etherates :



In the case of strong acids like sulphuric or perchloric acids however, the true oxonium salts are formed :



This theory was based on the results of investigations on the nature of undissociated acids using the following four methods :—

1. The examination of the absorption spectra of the acids, their salts and esters in different solvents and comparison of the curves so obtained.¹

¹ Hantzsch, *loc. cit.* ; Schäfer, *Z. anorg. Chem.*, (1917) 97, 285.

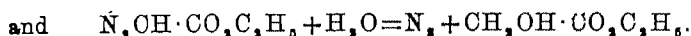
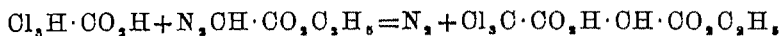
2. Measurement of the velocity of reaction with diazoacetic ester.¹ It has been seen that the pure acids, which contain no H-ions react very vigorously with the ester giving out nitrogen, and that the ethereal solutions of the fatty acids, which contain either the pseudo-acids themselves or their pseudo-etherates are inactive.

3. The velocity of inversion of cane sugar in aqueous solutions. This is a reaction attributed solely to the presence of H-ions and used even for the estimation of H-ion concentration. It has, however, been found that concentrated aqueous solutions of acids, even though not fully dissociated, can effect inversion of cane sugar more readily than fully dissociated acids.

4. The action of acids on indicators like dimethylaminoazobenzene. This is seen to be a function of the solvent and the concentration. Most of the organic solvents can make the acids completely inactive against indicators in sufficient dilution.

In view of these facts it was of some importance to follow up the changes, which take place when an acid goes into solution, from the thermochemical point of view.

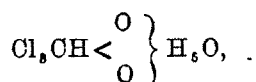
That the acids possess different properties in different solvents has often been shown. To give a well-known example, trichloroacetic acid reacts very vigorously with diazoacetic ester in pentane and water, giving out nitrogen according to the equations :



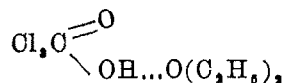
but is completely inactive in ethereal solutions even in quite moderate dilutions. Hantzsch explains this behaviour by the change in the constitution of the acid

¹ Dissertationen Leipzig, Teupel, Gutjahr, Schreiter, Karvė 1921-1924.

under the influence of the solvent. In aqueous solution we have the true hydroxonium salt



while in ether we have the pseudoetherate



Now, when an acid goes into solution, a certain amount of heat (generally positive) is evolved. This can be measured and represents the algebraic sum of the different energy changes taking place in the system. In the first place we have to consider the purely physical phenomena where the solvent acts like a diluent. The expansion of the original volume of the acid to that of the solvent and the consequent work done, the molecular dissociation of the acid and of the solvent, and in some cases the electrolytic dissociation, are all phenomena which normally absorb heat. If therefore no other chemical action took place between solvent and solute, every substance would possess a negative heat of solution. It must therefore be concluded that some combination between the acids and the solvents takes place, in order to explain the positive heat of solution. Especially in the case of solvents containing oxygen, these solvates are the oxonium salts (either the true ones or the pseudo). The heat of solution alone can give, of course, no clue to the constitution of the compound formed, which can only be ascertained by means of the action on diazoacetic ester and indicators. The measurements of heats of solution help us, however, to form an idea about the affinity between the two substances and also about the stability of the compounds formed.

The usual method for the determination of the heats of solution requires large quantities of substances and still the results are not very accurate, the data for the same two substances given by different authors being sometimes very different. The method used in the following determinations was very simple and gave consistent and reproducible results. The details are given in the experimental part.

1. *Sulphuric Acid.*

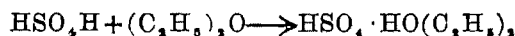
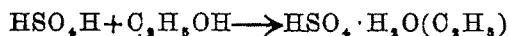
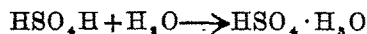
The following Table 1 gives the heats of solution of sulphuric acid in various solvents. The numbers in this and in other similar tables denote gram-calories per gram-mol of the solute.

TABLE 1.
Heats of Solution of Sulphuric Acid.

Mols solvent per mol acid	Water	Alcohol	Ether	Diethyl sulphate	Nitrobenzene
1	6200
2	9000
3	11200
5	18500	...	11380	2450	1200
10	15200	15000	12600	2900	1500
15	15800	15750	13600	3050	1700
20	16200	16400	14360	3250	1880
25	16400	16800	14960	3300	2000
40	16800	17500	2290
99	17800

It will be seen that the heats of solution in water, alcohol and ether are much higher as compared to those obtained in the other two solvents. This acid, as is already known

is very highly associated (compare Ramsay and Shields)¹ who give a value of $(\text{H}_2\text{SO}_4)_{32.3}$ and the formation of monomolecular solvates would naturally involve the process $(\text{H}_2\text{SO}_4)_n \rightarrow n\text{H}_2\text{SO}_4$, which would absorb a considerable amount of heat. The solvate-formation must therefore be a process which evolves a very great amount of heat. Kremann² has shown that at ordinary or even at slightly higher temperatures, no action takes place between sulphuric acid and ethyl alcohol and it was observed by me that ether and sulphuric acid do not react with each other even at 95° ; and as the solutions of the acid are found to be active towards diazoacetic ester and indicators, the compounds formed must be the true oxonium salts :



Compounds like these have often been shown to exist. Von Frank³ has proved the existence of an etherate of sulphuric acid containing equal number of molecules of the two substances, by means of the discontinuity of the vapour-pressure curve of mixtures containing them. Etherates of diethyl and diamyl ethers have even been obtained in crystalline form at very low temperatures.⁴ The acid is easily soluble in nitrobenzene and the determinations of molecular weight⁵ have shown that it is bimolecular. The relatively small heat of solution means naturally a very small tendency to salt-formation, and also the moderately "basic" nature of the oxygen

¹ J. Chem. Soc (1894), 65, 171.

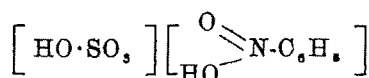
² Monatsh. (1910), 31, 1051.

³ Diss. Leipzig, 1923.

⁴ Tschelinzew and Koslow, J. Russ. Chem and Phys. Soc. (1914), 46, 708.

⁵ Ampola and Karlinfanti, Gazz. Chim. Ital. (1896), 26, II, 76.

in nitrobenzene. In spite of this, a definite compound has been isolated¹ at 0° which has probably the structural formula :



In order to observe whether the decrease in the association of the solvent, which is known to take place at higher temperatures² has any effect on the heat of solution, experiments were also made at different temperatures (in water at 0°, 10°, 20°, 30°, and 40°, in alcohol at 0°, 10°, 20° and 30°, and in ether at 0°, 10°, and 20°). It was observed that the decrease in the heat evolved was about 2% for every 10° in the case of water and alcohol, and that in the case of ether, which is known to be monomolecular at all temperatures, the heat evolved was practically constant.

The supposition that oxonium salts are present in these solutions, cannot be proved directly in the above instances. It could, however, be proved indirectly by means of the study of the absorption spectrum of diethyl sulphide in concentrated sulphuric acid. Diethyl sulphide or thioether is very similar to diethyl oxide or ordinary ether in chemical behaviour and constitution, and has the advantage of showing strong absorption in the ultraviolet region; the solution in sulphuric acid is, however, practically transparent just like trimethylsulphonium bromide $(\text{CH}_3)_3\text{SBr}$, the absorption of which has already been studied by Hantzsch.³ It can therefore be concluded that a similar compound also exists in the case of thioether having the formula $(\text{C}_2\text{H}_5)_2\text{SH} \cdot \text{O}_4\text{SH}$. By analogy, we can deduce the

¹ Cherbuliez, *Helv. Chim. Acta* (1923), 6, 281.

² Ramsay and Shields, *Z. Phys. Chem.* (1898), 12, 471.

³ Ber. (1919), 52, 1560.

structure of the compounds with water, alcohol and ether.

2. *The Halogen Acids.*

Thomsen's results¹ about the heats of solution of the three hydrogen halides are given below :

TABLE 2.

Heats of Solution of Hydrogen Halides in Water.

Mols water per mol acid	HCl	HBr	HI
1	5875
2	11365	13860	12540
3	13362	15910	14810
5	14959	17620	17380
10	16167	19100	18580
20	16756	19470	18990
50	17115	19820	19140

The values show that HI and HBr have a much greater affinity for water than HCl. In alcohol also, HBr is known to possess a higher heat of solution than HCl.² Hantzsch has shown by means of optical methods³ that HBr undergoes the following changes when dissolved in water :



oxonium

salt \longrightarrow hydration \longrightarrow ionisation

In the case of alcoholic and ethereal solutions, analogous phenomena can be assumed to take place, with the

¹ Landolt-Börnstein, Phys. Chem. Tabellen.

² Berthelot, Ann. chim. phys. (1876), 5, 9, 347.

³ Hantzsch, loc. cit.

difference that only HCl solutions of ether remain unchanged and allow the separation of definite etherates.¹ HBr acts upon ether slowly and HI very rapidly to form the respective ethyl esters and ethyl alcohol.² The observation of Jüttner,³ that the solubility of ether in water is increased by the presence of HCl, can be explained on the assumption that the etherate of HCl, having the nature of a salt, will naturally be more soluble in water than ether itself.

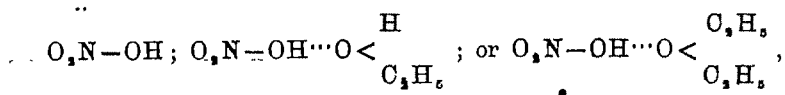
3. Nitric Acid.

TABLE 3.

Heats of Solution of Nitric Acid.

Mols solvent per mol acid	Water	Alcohol	Ether
5	6685	—	8600
10	7318	5750	9080
15	7400	7500	9340
20	7458	8450	9440
25	7480	8750	9480
30	7490	9000	9500

The results of the investigations on the optical behaviour of nitric acid can be summarised as follows : In dilute aqueous solutions the ultraviolet absorption is the same as that of the solutions of the nitrates, and contain the true hydroxonium salt $\text{NO}_3 \cdot \text{H}_2\text{O}$; the alcoholic and ethereal solutions as well as the pure acid have an absorption very similar to that of the esters and hence these have the pseudo-formula :

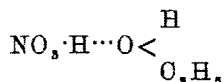


¹ Steele, McIntosh and Archibald, *Z. Phys. Chem.*, (1909) 55, 152.

² Silva, *Ber.*, (1876) 9, 852,; Lippert, *Ann. d. Chem.*, (1893) 276, 148.

³ *Z. phys. Chem.*, (1901) 88, 56.

The heat of solution in either alcohol or ether can therefore be taken to be the heat of formation of the pseudo-salt. The heat of solution in water is much smaller than in ether, and as the true hydroxonium salt is present in aqueous solutions, the transformation of the pseudo-acid into the true acid appears to be an endothermic process. The heat of solution in alcohol is slightly smaller than in ether and it shows, in agreement with the results of the optical investigation, that although the greater portion of the acid is present as a pseudo-salt, a very small percentage is still present as the true salt :



and has a lower heat of formation.

In ethyl and methyl nitrate, the acid dissolves without any heat of solution, and consequently with no change in the constitution.

4. *Formic Acid.*

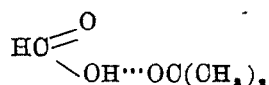
TABLE 4.

Heats of Solution of Formic Acid.

Mols solvent per mol acid	Water	Alcohol	Ether	Acetone	Ohloroform
5	...	670	1285	1860	-250
10	...	950	1305	2020	-320
15	...	980	1875	2180	-360
20	...	970	1420	2220	-390
25	..	990	1480	2300	-410
* Mols of Solvent necessary for inactivation.	...	20	10	9.2	...

* The last horizontal column in the table shows the amounts of the various solvents in mols which were required, to make one mol of the acid inactive against diazoacetic ester and indicators. The acid is then supposed to be completely transformed into the pseudo-form.

It is very remarkable that the heat of solution in water is so low that it could not be measured. The pure acid has been shown to contain¹ about 95% of the pseudo-acid and about 5% of true acid in equilibrium. The aqueous solution contains however much more of the true hydroxonium salt and we have to conclude that the dissociation of the acid absorbs very nearly the same amount of heat as is evolved by the formation of the salt. The highest heat is evolved in acetone solutions; and it is also this very solvent which "inactivates" the acid in the most concentrated solution. The heat of solution is therefore the heat of formation of the pseudo-salt:



Similarly the heats of solution in alcohol and ether are the heats of formation of the respective pseudo-salts.

5. *Acetic Acid.*

TABLE 5.

Heats of Solution of Acetic Acid.

Mols solvent per mol acid	Water	Alcohol	Ether	Acetone	Ethyl acetate	Benzene	Pentane
5	-80	...	+45	+650	...	-500	-1000
10	+35	..	+33	740	+51	-760	-1220
15	+115	...	+22	810	+24	-800	-1360
25	+208	900	...	-970	-1510
50	+275		...	980	.	..	-1660
Mols of solvent necessary for inactivation	5.1	2.2

¹ Hantzsch, *loc. cit.*

All the heats of solution are comparatively very small. In concentrated aqueous solutions the heat absorbed by the dissociation appears to be greater than the heat evolved by the formation of the hydroxonium salt; in dilute solutions, however, more of the salt is formed and an evolution of heat is observed. In the case of acetic acid also, the heat of solution in acetone is the highest, and this solvent also inactivates the acid most easily. Benzene and pentane, as fully saturated compounds, have very little or no tendency to solvate-formation, and the negative heat of solution is to be attributed solely to physical causes.

6. *Trichloroacetic Acid.*

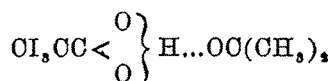
TABLE 6.

Heats of Solution of Trichloroacetic Acid (liquid).

Mols solvent per mol acid	Water	Alcohol	Ether	Acetone	Benzene	Pentane	Nitrobenzene
5	1050
10	...	1270	...	5170	...	-6250	-800
20	...	1450	1310	5320	...	-6000	-460
30	...	1570	1550	5410	-6600	-5850	-120
40	400	1675	1690	5470	-6220	-5750	+100
50	800	1760	1790	5520	-5750	-5670	+350
100	2030	2130	2000	...	-5320	-5320	...
Mols of solvent necessary for inactivation	27	253	35

¹ The pure crystalline acid was used in all these experiments, and the known heat of fusion deducted from the heat measured, thus giving the heat of solution for the liquid acid.

The heat of solution in water is comparatively small, and the heats of solution in solvents not containing oxygen are negative. It is to be expected that the dissociation absorbs a great amount of heat, and at least in concentrated aqueous solutions, this heat is equal to the heat of formation of the true hydroxonium salt. In dilute solutions, the heats of solution are very nearly equal in solvents like water, alcohol and, ether, and the formation of the true as well as of the pseudo-salt appears to evolve the same amount of heat. The highest heat of solution is observed in acetone, although unlike formic and acetic acids, it is ether which inactivates the acid most easily. It has to be assumed, therefore, that acetone forms a true salt with trichloroacetic acid, having the formula:



Some experiments were also made to determine the heats of solution of various substances in concentrated sulphuric acid, (99%), the results of which are given in Table 7.

TABLE 7.

Heats of Solution in Sulphuric Acid.

Mols H ₂ SO ₄ per mol solute	Water	Methyl alcohol	Ethyl alcohol	Ether	Thio- ether	Acetic acid	Nitric acid
5	10740	...	11600	9580	...
10	11300	13900	12230	17070	14900	9900	7200
15	11700	14700	12500	17200	15200	10100	7850
20	11890	14800	12660	17370	15400	10220	8250
25	12120	14840	12780	17520	15600	10320	8550
30	..	14860	12880	17640	15800	10450	8750
50	...	14900	13160	17900	16340	10820	...

Here the acid is present in such large excess, that practically the whole of the solute might be said to be present in the form of a compound with the acid, and hence the heats evolved are the heats of formation of the various compounds. The comparatively small increase in the heat evolved, with increasing amounts of the solvent can thus be easily explained, while even in the most concentrated solutions, practically the whole of the solute has combined with the acid.

Ether possesses the highest heat of solution, and this shows that the diethyloxonium sulphate $\text{HSO}_4 \cdot \text{HO}(\text{C}_2\text{H}_5)_2$ has the highest heat of formation. Thioether has only a slightly lower heat of solution and shows once more the similarity in the behaviour of oxygen and sulphur compounds. As sulphuric acid is known to be active towards diazoacetic ester and indicators in all solvents, the compounds formed in all the above cases are the true salts. The fact that pure nitric acid has a positive heat of solution, can only be explained by means of the assumption that in comparison with more strongly acidic sulphuric acid, nitric acid functions as a "base." In the case of acetic acid, this is still more pronounced.

EXPERIMENTAL.

A. The calorimeter used for the experiments described above was of very simple construction. A small test tube was fitted up into another slightly larger one by means of a thin cork, and served as the actual calorimeter. The thermometer used was a standard one reading to one-tenth of a degree. The stirrer was a capillary tube drawn out and bent circular at the lower end. It was calibrated along the whole of its length, and was also used as a pipette to deliver known volumes of the liquid, whose heat of solution was to be measured,

into the calorimeter. The method was as follows: 10 c.c. of the solvent were taken into the calorimeter and after the temperature had become constant, a known volume of the acid was introduced by means of the stirrer-pipette. The solution was stirred uniformly and the maximum or the minimum temperature noted. With the help of the water-equivalent of the calorimeter, thermometer and stirrer, which had previously been determined by measuring the heat of neutralisation of dilute hydrochloric acid with alkali, and of the specific heat of the solvent, which was taken to be equal to that of the dilute solution, the total heat evolved or absorbed was calculated according to the formula :

$$Q = \{w \times (t_2 - t_1)\} + \{10ds \times (t_2 - t_1)\}$$

were

w = water equivalent, t_1 = initial temperature,

t_2 = final temperature, d = density of the solvent, and

s = specific heat of the solvent.

About 10 experiments were made in the case of each acid and the results plotted on graph paper, taking the mols of solvent per mol of solute as ordinates and the heat of solution per mol of solute as the abscissa. The numbers given in Tables 1-7 were then obtained by graphical interpolation.

B. The experiments on the inactivation of the acids were made as follows: Weighed portions of the acid and the calculated amounts of ethyl diazoacetate were brought together and dissolved in increasing quantities of the solvent until there was no evolution of nitrogen for 24 hours. This quantity of solvent was then taken to be the amount necessary to transform the acid completely into the pseudo-form. It was found to be practically identical

Effect of Light on the Interaction of Water and Sodium and Potassium Amalgams (preliminary).

By

S. S. BHATNAGAR, MATA PRASAD

AND

D. M. MUKERJI.

The action of water on sodium and potassium Amalgams has been studied by Berthelot (Compt. rend., 88, 1108) and Kerp (Zeit. anorg. Chem., 1898, 17, 284). Parker (Trans. Chem. Soc., 1913, 103, 2060) studied the rate of reaction of variously treated waters on Sodium Amalgams and found that the activity is enormously increased by the addition of Hydrogen Peroxide. Muller and Riedel (Zeitsch. Elektrochem., 1920, 26, 104) found that the activity was also accelerated in the presence of iron alloys of Molybdenum, Chromium, etc.

Early investigators have shown that alkali metals emit electrons when they are exposed to ultra-violet light or ordinary visible light. Elster and Geitel discovered in 1894 that liquid alloys of Sodium and Potassium exhibited the property of selective Photo-Electric Effect. They also found that in such cases the number of electrons emitted had a maximum value for a particular frequency of light. Maximum effect in case of potassium occurs at $440\mu\mu$ and at $340\mu\mu$ in case of sodium (*cf.* Hughes' Photo-electricity). The same effect was also observed to take place when the metals were in the colloidal state.

The authors undertook this investigation with a view to examine the behaviour of alkali metals (Sodium and Potassium) under the action of light when they are present in combination with mercury in the Amalgams in the liquid state. To observe any effect that may be produced on exposure to light, the interaction of water and Amalgams in presence of light has been studied on account of its being the simplest and least complex chemical action.

EXPERIMENTAL.

Amalgams experimented upon were liquid Sodium and Potassium Amalgams. They were prepared by the electrolytic method of T. W. Richards (J. Amer. Chem. Soc., 1922, 44, 601) and were kept in storing vessel out of contact with air where they did not alter in composition for about a fortnight (*cf.* Bhatnagar, Prasad and Mukerji Surface Tension of Amalgams at the Amalgam-Benzene interface J. I. C. S. 1924, 1, 81); The storing vessel was wrapped in a cloth to protect the Amalgams from exposure to light.

The interaction of water and Amalgams was allowed to take place in an optically correct cell A of quartz. It was fitted with an air-tight rubber stopper through which passed a tube B to add water and a tube C to carry the gas evolved to the burette D where it was collected over water under reduced pressure as shown in the figure.

For each experiment about 3 c. c. of the Amalgam were taken out of the storing vessel in a small tube which was completely covered with black paper to protect the Amalgam from being exposed to light. The Amalgam was poured into the reaction cell A which was immediately closed with a rubber cork. The amount of the Amalgam taken for experiment was quite sufficient to cover the bottom of the reaction cell completely.

The cell was then placed in a thermostat maintained at a constant temperature of 40°C. It was kept immersed in the bath for about 5 minutes to acquire the temperature of the bath before any reaction was started. To allow the passage of light through it to the reaction cell, the thermostat carried glass panes on its sides.

To observe the rate of reaction in the dark, the cell was well covered with black paper and black cloth. Light from carbon arc, giving out rays of wave-lengths varying from $210\mu\mu$ to $700\mu\mu$ was used as the source of light. It was always kept at a fixed distance from the thermostat. Also the reaction vessel was kept at a fixed distance from the side of the thermostat in order that the amount of absorption of rays in their passage through the glass panes and water may be the same in each case. The effective wave-lengths of the arc-light were known by taking a spectrum photograph of the light passing through the same thickness of water and glass as in the experiment by means of an Adam Hilger Spectrograph. It was found that the light of the arc falling on the surface of the reactants comprised of wave-lengths ranging from $366\mu\mu$ to $525\mu\mu$.

5 c. c. of pure distilled conductivity water were added to the reaction vessel through the tube B and the gas evolved was measured in the burette after an interval of every 6 minutes. The temperature and the barometric pressure at which the gas was collected, were noted and the volumes were reduced to N. T. P.

For each different Amalgam the readings were first taken in darkness and then on exposure to arc-light. In the latter case the reaction cell with the Amalgam was kept exposed for 5 minutes before the water was dropped in and the initial observation in the burette was taken. Thus any disturbance due to the expansion of air

of the reaction vessel owing to the heating effect of the are light was eliminated.

The composition of Amalgams was determined by allowing a known amount of Amalgams to react with water and then titrating the alkali (Sodium or Potassium Hydroxide) with standard solution of Hydrochloric Acid. The quantities of Sodium or Potassium present in the Amalgam were then calculated in grams per cent. of the Amalgam.

The effect of light produced on Amalgams containing varying quantities of Sodium or Potassium has been brought out in the following tables :—

TABLE I.

*Concentration of Sodium in the Amalgam = 0.081
gms. % .*

DARK.		LIGHT.	
Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecu- tive intervals of 6 minutes.	Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecu- tive intervals of 6 minutes
0.67 c.c.	0.67 c.c.	0.88 c.c.	0.88 c.c.
1.08 "	0.41 "	1.35 "	0.47 "
1.35 "	0.27 "	1.66 "	0.31 "
1.53 "	0.18 "	1.97 "	0.31 "
1.72 "	0.19 "	2.20 "	0.23 "
1.91 "	0.19 "	2.45 "	0.25 "
2.13 "	0.22 "	2.68 "	0.18 "
2.31 "	0.18 "	2.79 "	0.16 "
2.48 "	0.17 "	2.96 "	0.19 "
2.56 "	0.08 "	3.11 "	0.13 "

TABLE II.

Concentration of Sodium in the Amalgam = 0.158 grams %

DARK.		LIGHT.	
Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecu- tive intervals of 6 minutes.	Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecu- tive intervals of 6 minutes.
0.51 c.c.	0.51 c.c.	0.77 c.c.	0.77 c.c.
0.86 "	0.35 "	1.14 "	0.37 "
1.12 "	0.26 "	1.45 "	0.31 "
1.34 "	0.22 "	1.68 "	0.23 "
1.54 "	0.20 "	1.92 "	0.24 "
1.74 "	0.20 "	2.18 "	0.26 "
1.92 "	0.18 "	2.45 "	0.27 "
2.11 "	0.19 "	2.69 "	0.24 "
2.33 "	0.22 "	2.95 "	0.26 "
2.55 "	0.22 "	3.25 "	0.30 "

TABLE III.

Concentration of Sodium in the Amalgam = 0.214 gms. %

0.54 c.c.	0.54 c.c.	0.98 c.c.	0.98 c.c.
0.84 "	0.30 "	1.53 "	0.55 "
0.98 "	0.14 "	1.97 "	0.44 "
1.17 "	0.19 "	2.36 "	0.39 "
1.40 "	0.23 "	2.62 "	0.26 "
1.61 "	0.21 "	2.88 "	0.21 "
1.73 "	0.12 "	3.05 "	0.22 "
1.90 "	0.17 "	3.23 "	0.18 "
2.12 "	0.22 "	3.43 "	0.20 "
2.34 "	0.22 "	3.82 "	0.39 "

TABLE IV.

Concentration of Sodium in the Amalgam = 0.311 gms. %.

DARK.		LIGHT.	
Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecu- tive intervals of 6 minutes.	Total volumes of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecu- tive intervals of 6 minutes.
0.46 c.c.	0.46 c.c.	1.37 c.c.	1.37 c.c.
0.88 "	0.87 "	2.17 "	0.80 "
1.21 "	0.88 "	2.84 "	0.67 "
1.64 "	0.43 "	3.46 "	0.62 "
2.04 "	0.40 "	4.03 "	0.57 "
2.29 "	0.25 "	4.27 "	0.24 "
2.50 "	0.21 "	4.46 "	0.19 "
2.75 "	0.25 "	4.76 "	0.30 "
3.02 "	0.27 "	5.09 "	0.33 "
3.31 "	0.29 "	5.33 "	0.24 "

TABLE V.

Concentration of Potassium in the Amalgam = 0.038 gms. %.

0.54 c. c.	0.54 c. c.	0.76 c. c.	0.76 c. c.
0.84 "	0.30 "	1.20 "	0.44 "
1.12 "	0.28 "	1.56 "	0.36 "
1.40 "	0.28 "	1.92 "	0.36 "
1.68 "	0.23 "	2.16 "	0.24 "
1.86 "	0.23 "	2.48 "	0.32 "
2.05 "	0.19 "	2.77 "	0.29 "
2.21 "	0.16 "	3.10 "	0.33 "
2.37 "	0.16 "	3.42 "	0.32 "
2.52 "	0.15 "	3.63 "	0.21 "

TABLE VI.

Concentration of Potassium in the Amalgam = 0.041 gms. %

DARK		LIGHT	
Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecutive intervals of 6 minutes.	Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecutive interval of 6 minutes.
0.63 c. c.	0.63 c. c.	0.83 c. c.	0.83 c. c.
1.07 "	0.44 "	1.54 "	0.71 "
1.50 "	0.43 "	2.06 "	0.52 "
1.84 "	0.34 "	2.61 "	0.55 "
2.18 "	0.34 "	2.99 "	0.38 "
2.48 "	0.30 "	3.35 "	0.36 "
2.76 "	0.28 "	3.68 "	0.33 "
3.01 "	0.25 "	4.02 "	0.34 "
3.28 "	0.27 "	4.35 "	0.33 "
3.49 "	0.21 "	4.61 "	0.26 "

TABLE VII.

Concentration of Potassium in the Amalgam = 0.056 gms. %

0.60 c. c.	0.60 c. c.	1.17 c. c.	1.17 c. c.
1.28 "	0.68 "	991 "	0.82 "
1.80 "	0.52 "	2.60 "	0.61 "
2.28 "	0.48 "	3.11 "	0.51 "
2.76 "	0.48 "	3.63 "	0.52 "
3.23 "	0.47 "	4.01 "	0.40 "
3.65 "	0.42 "	4.32 "	0.29 "
3.99 "	0.34 "	4.62 "	0.30 "
4.31 "	0.32 "	4.85 "	0.33 "
4.69 "	0.38 "	5.23 "	0.28 "

TABLE VIII.

Concentration of Potassium in the Amalgam = 0.101 gms. %.

DARK		LIGHT	
Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecutive intervals of 6 minutes.	Total volume of gas (reduced to N. T. P.) accumulated at intervals of 6 minutes.	Volume of gas (reduced to N. T. P.) evolved in consecutive intervals of 6 minutes.
0.66 c. c.	0.66 c. c.	1.81 c. c.	1.81 c. c.
1.48 "	0.80 "	2.28 "	0.97 "
2.21 "	0.75 "	3.02 "	0.74 "
2.80 "	0.59 "	3.63 "	0.61 "
3.32 "	0.52 "	4.13 "	0.50 "
3.80 "	0.48 "	4.60 "	0.47 "
4.14 "	0.34 "	5.05 "	0.45 "
4.55 "	0.41 "	5.45 "	0.40 "
4.98 "	0.43 "	5.92 "	0.47 "
5.34 "	0.36 "	6.28 "	0.36 "

Discussion of Results.

It will be seen from the Tables I-VIII that in all cases the rate of evolution of the gas (hydrogen) by the action of Amalgams on water is increased by the presence of light. The total increase in volume of the gas evolved in an hour on change of Sodium and Potassium content of the Amalgam is indicated in the following Tables.

TABLE IX.

Sodium Amalgams.

Quantity of Na in 100 gms. of Amalgam.	Increase in volume of the gas in one hour.
0.081 gms.	0.55 c. c.
0.158 "	0.70 "
0.214 "	1.48 "
0.301 "	2.52 "
0.311 "	20.2 "

TABLE X.

Potassium Amalgams.

Quantity of K in 100 gms. of Amalgam	Increase in volume of the gas in one hour.
0.038 gms.	1.11 c. c.
0.041 "	1.12 "
0.056 "	1.54 "
0.101 "	0.94 "

The above Tables show that the difference in volume of the gas evolved in light and in darkness increases as the amount of Sodium or Potassium in the Amalgam is increased up to a certain point. After that point the difference decreases on further increasing the concentration of Sodium or Potassium. These latter points lie on a different branch of the curve obtained by plotting the amount of Sodium or Potassium in 100 grams of the Amalgam against increase in volume.

Authors, while determining the Interfacial Tension of Sodium and Potassium Amalgams against Benzene, found that these points lay on different straight lines obtained by plotting the quantities of Sodium or Potassium in 100 grams of the Amalgam against interfacial Tensions (*cf.* Bhatnagar and Prasad and Mukerji, *loc. cit.*).

From the foregoing Tables it is clear that the activity of Sodium and Potassium Amalgams is accelerated in the presence of light. This increase in the activity may be due to the emission of electrons by Sodium and Potassium present in the Amalgams. The reaction, according to Einstein (*Ann. d. Physik*, 1912, (4) 37, 832), Landesberg (*Journ. Russ. Phys. Chem. Soc.* 1915, 47, 908),

and others, is a photochemical one and it is proposed to investigate it further from the view-point of Einstein's Photochemical equation.

Wiedmann (Ber. d. Deutsch. phys. Gesell, 1916, 18, 333), has found that to produce selective photo-electric effect in Potassium, the presence of Hydrogen gas is essential. Photo-electric effect, whether selective or normal (*cf.* Millikan and Sonder, Proc. Nat. Acad. Sci, 1916, 2, 19), might have been produced in this case by the presence of the Hydrogen gas evolved in the reaction.

The reaction of Amalgams on water takes place in the dark as well, but not to the same extent as in light. It has been pointed out by Baly (Physikal. Zeitsch. 1913, 14, 893), Henri and Würmser (Journ. d. Physique, (5) 1913, 3, 305), that in cases¹ of substances dissolved in a solvent, the reaction is accelerated and not initiated by light. These Amalgams have also been shown to belong to the same category.

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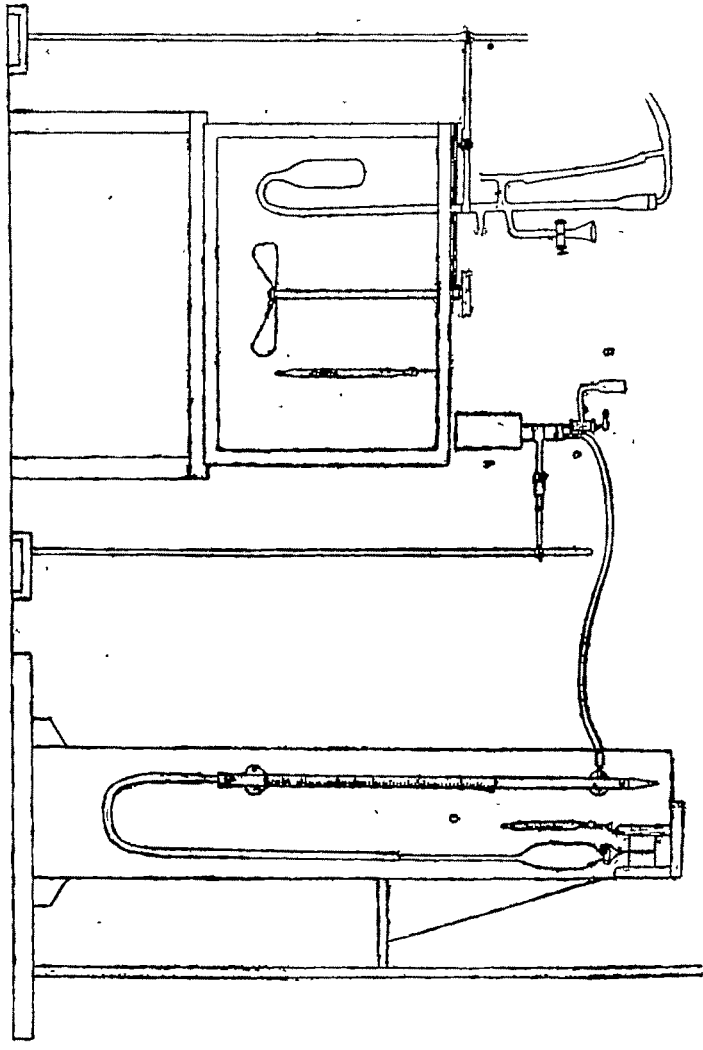
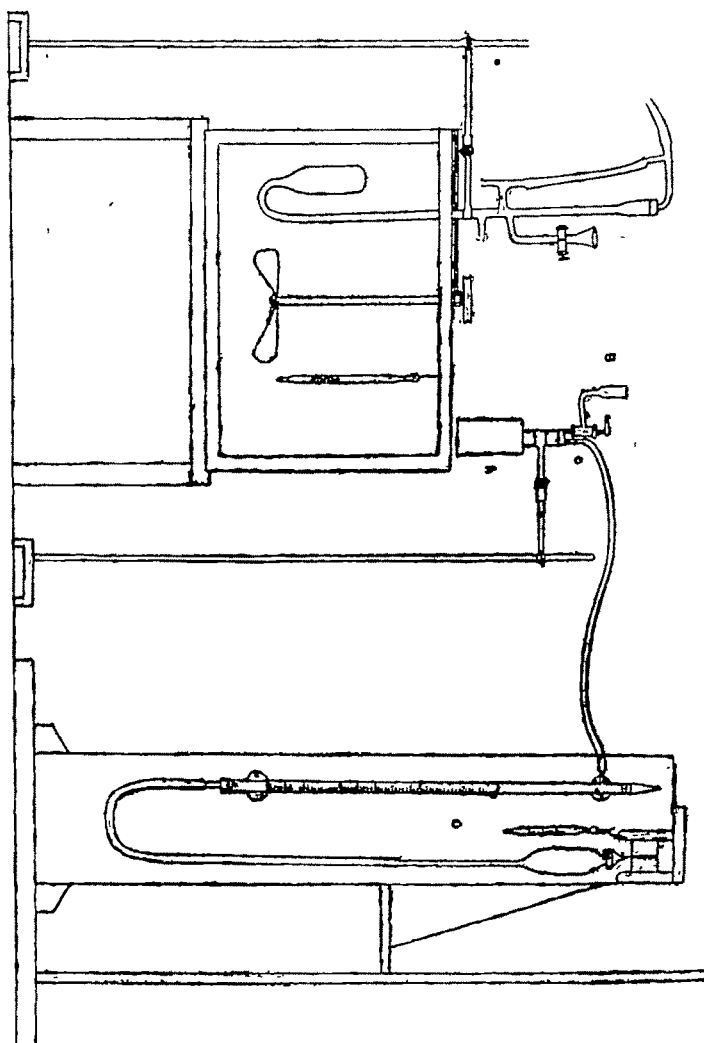


FIG. 1

Fig. 1



Travancore Essential Oils.

Part V.

Essential Oil from *Ageratum conyzoides*, Linn:

(Appa Grass)

BY

KISHORI LAL MOUDGILL.

Preliminary Note.

(1) This plant is a member of the Compositae and grows wild in all places in Travancore to such an extent that it is looked upon as a pest and its growth is checked as far as possible. It is known in Trivandrum as *Muryan Pacha* (destructive green or grass), a name which is very significant. The vernacular name for the weed varies from place to place and the author got to know of it first as *Appa* grass. It can be easily distinguished by its characteristic white flowers which possess a pleasant and sweet aroma.¹ The leaves and the flowers yield an essential oil which is slightly heavier than water and possesses a powerful, almost nauseating, odour which is very persistent and, on very great dilution, resembles remotely the aroma of fresh mown hay. This explains the contrast between the strong odour of the oil and the pleasant aroma of the flowers and leaves in which the oil is very much diluted.

Appa oil appears to be simple in composition and contains about 90 per cent. of a compound, $C_{13}H_{16}O_2$, which is under investigation.

¹ I am obliged to Mr Vencaba Rao, the Curator of the Herbarium in the Forest Department, for the botanical note which is reproduced at the end of this paper. (page 276).

According to Murat¹ (Parry, Chem. of Ess. oils and Art. Perf., Vol. I, page 302) 500 kilos of this plant distilled with steam in Annam gave 27 grams of oil.

EXPERIMENTAL.

Five hundred pounds of the freshly cut plant (moisture = 87 per cent.) were distilled with steam in a large copper still provided with a false bottom so that the plant should not come in contact with the hot surface, and the oil was collected in receivers designed for light oils and heavy oils arranged in series. About 45 c.c. of a dark brown, heavy oil were collected in the first receiver. The other receivers contained about 5 c.c. of a lighter oil; but owing to the comparatively large size of the vessels this oil had to be extracted with ether, and as the quantity obtained was too small for experiments nothing further was attempted. The colour of the heavy oil is due to a pigment and can be got rid of by distillation. The constants are given below:—

TABLE I.

	Moudgill.	Murat.
Yield (fresh grass) ..	0.02 per cent.	0.0034 per cent. (?)
" (dry grass) ...	0.16 per cent.
... ..	invisible	—1° 20
n_D^{25}	1.5280
Acid value	0	0.9
Ester value	17.4	12.1
Acetyl value	45.6 ²
d_4^{25}	1.008

¹ Parry does not give a reference to the original paper by Murat.

² The end-point of the titration was not sharp owing to the presence of the pigment referred to above which seems to undergo a colour change on boiling with alcoholic caustic potash.

A small quantity of the oil (18 c.c.) was distilled under reduced pressure and two fractions, possessing the following constants, were obtained.

TABLE II.

No.	B. pt.	†Yield.	$[\alpha]_{\text{D}}^{28^\circ}$	$n_{\text{D}}^{28^\circ}$	$d_{4^\circ}^{28^\circ}$
1	180°–185°/19 mm. ...	77%	$\pm 0^\circ$	1.5293	1.019
2	Above 185° ...	12%	...	1.5283	...
3	Residue (by difference)

A portion of the first fraction was distilled from a small bulb without decomposition.

B. pt. 254°–256°/756 mm. $n_{\text{D}}^{28^\circ}$ 1.5298.

It would appear, therefore, that the major portion of Appa oil consists of a liquid having the following characters :—

B. pt. at 19 mm. ... 130°–135°

„ at 756 mm. ... 254°–256°

$d_{4^\circ}^{28^\circ}$... 1.019

$[\alpha]_{\text{D}}^{28^\circ}$... $\pm 0^\circ$

$n_{\text{D}}^{28^\circ}$... 1.5298

Found: C = 73.87; H = 8.72 per cent. $\text{C}_{12}\text{H}_{16}\text{O}_2$ requires
C = 74.43; H = 8.27 per cent.

† As the quantity of the oil used for fractionation was very small, the yields given above are not a very accurate measure of the proportions of the constituents. The second fraction consists very largely of the compound in fraction 1.

From its properties and constants the compound appears to be an oxide of the formula $C_{12}H_{16}O_2$, but further work is in progress and this formula is advanced only tentatively. It has not been possible to obtain the oil in quantity owing to the low yield and the difficulty of collection of the plant, but as the oil is rich in oxygenated compounds and contains only a small proportion of hydrocarbons, a more detailed investigation with larger quantities of the oil will be undertaken in August, 1925, when the plant will be in season.

The author wishes to thank Mr. I. C. Chako, Director of Industries, for defraying the cost of distillation and collection and for other help.

BOTANICAL NOTES.

Ageratum conyzoides, Linn., Annual, one to two feet high, hispidly hairy leaves, petioled, ovate, crenate, head small in dense terminal corymbs, bracts striate acute, ray flowers many, pale blue or white, achenes black, pappus scales 5 awned often serrate below.

Synonym: *Ageratum cordifolium*, Roxb., distribution throughout India, ascending the Himalayas to 5000 feet. All hot countries.

CHEMISTRY DEPARTMENT,

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(Received, December 23, 1924.)

Reactivity of the Methylene group in Coumarin-4-acetic acids.

Part II.

Condensation with aromatic aldehydes to coumaryl phenyl ethylenes.

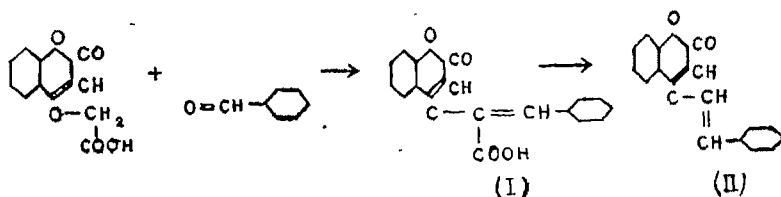
BY

BIMAN BIHARI DEY

AND

KARNAD KRISHNA ROW.

It has been shown (J. Ind. Chem. Soc., Vol. I, 107) that coumarin-4-acetic acids and their ethyl esters condense with salicylaldehyde, to form a new class of bodies which have been named 4:3'-dicoumaryls. The study of this reaction has now been extended to other aromatic aldehydes, and in a few cases the parallel condensations with phenyl-acetic acid have also been examined. The products are of the stilbene type in which one of the phenyl groups has been replaced by the coumarin nucleus, the latter being attached at the 4-position to the ethylene carbon atom. The reactions proceed thus:



The carboxylic acids (I) frequently split off carbon dioxide during the reaction giving the free ethylene derivatives (II), and this is found to happen much more readily if the experiment is carried out under the conditions of Knoevenagel's reaction than by Perkin's method.

The nature of the product ultimately obtained, however, depends largely on the stability of the acids (I) at the temperature of the experiment. Thus, the product obtained from vanillin and phenylacetic acid by heating at 140° in the presence of piperidine was found to consist mainly of the α -free ethylene derivative (II), whilst piperonal under the same conditions and at a considerably higher temperature (170°), gave chiefly the carboxylic acid (I), and only a minute quantity of the CO_2 -free product. Coumarin-4-acetic acids, as a class, split off carbon dioxide completely at their melting points (Dey, T., 1915, 107, 1610), and this decomposition is found in some cases to have begun at a much lower temperature. The instability of these acids, therefore, constituted a serious obstacle to the progress of this work. As the reaction depended solely on the presence of the methylene group in the acid, it could obviously not proceed at all if carbon dioxide were split off prior to the condensation. Attempts to stabilise the carboxyl-group by esterification did not lead to the desired result as the curious fact came to light that the esters were remarkably unreactive bodies and would not condense at all with aldehydes in the presence of piperidine, although under exactly the same conditions they gave with salicylaldehyde an almost quantitative yield of the 4:3'-dicoumaryls (*loc. cit.*). We cannot say we have been very successful in our attempts to solve the problem of controlling the process so that the decomposition of the acids to the 4-methyl-pyrone would be reduced to a minimum and this condensation with aldehydes to the coumaryl-phenyl-ethylene raised to a maximum, but as a general rule, satisfactory results were obtained only when the temperature was maintained as far below the fusion points of the acids as was compatible with the initiation of the reaction. Even then the formation of considerable amount of the pyrone could not

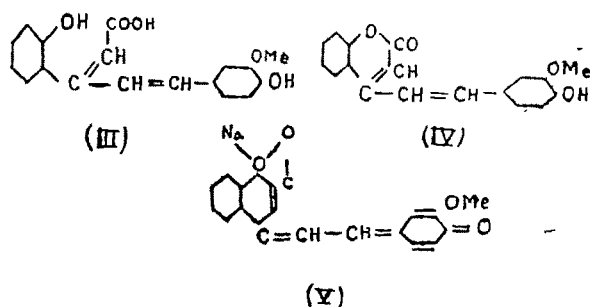
be avoided, and its separation was found to be much more difficult than could be anticipated.

Attention was next directed towards effecting the condensation with such aldehydes as would permit of the products being separated chemically from the corresponding 4-methyl-pyrones. Thus vanillin and *p*-dimethyl-amino-benzaldehyde condensed with coumarin-4-acetic acids to form the corresponding *p*-hydroxy, and *p*-dimethyl-amino-phenyl-coumaryl ethylene derivatives respectively which could be readily purified by extracting with cold dilute alkalis or acids.

The product from vanillin and 7-methyl-coumarin-4-acetic acid seems to be of some interest on account of the remarkable colour changes which it undergoes in alkaline solution. The compound, which has a bright yellow colour, dissolves in cold dilute caustic alkalis with a deep red colour, and on acidification, the original substance is precipitated unchanged. If, however, the alkaline solution be allowed to stand at the ordinary temperature (30°C), the colour gradually fades, and in the course of about half an hour the deep red solution becomes practically colourless. The same change is found to occur in about a minute, if the solution be warmed in the water-bath. On cooling and acidifying this solution, a milky emulsion is produced which dissolves immediately in cold dilute sodium carbonate to a clear colourless solution. On standing, however, at the ordinary temperature or even at 0°, the emulsion slowly changes into yellow crystals of the original substance, which then dissolves in dilute caustic soda with the same deep red colour as was observed before. The change of the emulsion into the yellow solid is greatly accelerated by warming.

The interesting point that emerges out of a study of this cycle of changes is that the milky solid obtained by

neutralising the colourless alkaline solution dissolves immediately in cold sodium carbonate solution, although the original substance is insoluble in this medium. The presumption, therefore, seems to be most reasonable that the former is an unstable acid of the coumarinic type (III) which is only stable in alkaline solution and in the presence of acid readily reverts to the original coumarin (IV), the deep colour of which in alkaline solution may be explained if it is permissible to assume that the pyrone oxygen atom of the coumarin ring can become quadrivalent (*cf.* Dey T., 1915, 107, 1622; also Homfrey T, 1905, 87, 1453); the molecule tantomerising to a form which is quinonoid both in the pyrone and vanillin nuclei (V).



This view would seem to receive further support from the following observations :

(1) If the original yellow compound is dissolved in dry benzene and then treated with metallic sodium, the solution assumes a deep red colour which does not disappear even on boiling.

(2) An alcoholic solution of sodium ethoxide dissolves the compound with a deep red colour, the solution assuming a pale yellow tint only on boiling for sometime.

(3) The corresponding compound from vanillin and phenyl-acetic acid, which is colourless, dissolves in cold dilute caustic soda without any colour, and there is no

perceptible change either on standing or boiling the solution.

These experiments, therefore, furnish clear evidence in favour of the idea that the changes in colour are caused by the opening of the pyrone ring for which the presence of water or alcohol is indispensable: in dry benzene no change in colour takes place. Attempts are now being made to synthesise and study more closely other compounds of a similar type with a view to throw further light on this question.

EXPERIMENTAL.

A. COUMARYL-PHENYL-ETHYLENES.

7-methyl-4-coumaryl-p-methoxy phenyl-ethylene.

2.8 Grams of freshly distilled anisaldehyde and 4 grams of pure 7-methyl-coumarin-4-acetic acid were mixed in a small flask, 8-10 drops of piperidine added, and the mixture heated in an oil-bath at 130°-135° under air reflux for four hours. On cooling, the solid mass was extracted several times with small amounts of hot rectified spirit, and the yellowish residue crystallised once from acetic acid and then from absolute alcohol. Pale yellow needles were obtained melting at 180°, and dissolving in cold concentrated sulphuric acid with a deep red colour in the characteristic manner of the stilbenes (Found: C=78.50; H=5.62. $C_{19}H_{16}O_3$ requires C=78.08; H=5.48 per cent.)

α -naphthapyrone-4-p-methoxyphenyl ethylene.

This was prepared in the usual way from anisaldehyde (2.5 grams) and α -naphthapyrone-4-acetic acid (4 grams) by heating to 125°-130° for three hours. The brownish residue left after washing the dark product with alcohol, when recrystallised twice from boiling glacial acetic acid,

formed bright yellow needle-shaped crystals, m.p. 182° - 83° C. It gave the usual red colour with strong sulphuric acid, and readily decolourised a solution of bromine in chloroform. (Found: C=80.14; H=4.48. $C_{22}H_{16}O_3$ requires C=80.48; H=4.87 per cent.)

*7-methyl-4-coumaryl-3'-methoxy-4'-hydroxy phenyl
ethylene.*

Vanillin (3 grams), and 7-methyl-coumarin acetic acid (4 grams) were heated in the usual way for 3-4 hours at 140° , the hot melt transferred to a dish and washed three times with 10 c.c. of cold methylated spirit. The residue was then extracted with cold decinormal caustic soda and the dark red filtrate acidified. A dark gummy mass was precipitated, which on rubbing with a little cold alcohol, changed into a hard crystalline powder. Two crystallisations from fifty per cent. acetic acid gave golden yellow needles melting sharply at 222° . (Found: C=74.52; H=5.48. $C_{18}H_{16}O_4$ requires C=74.02; H=5.19 per cent.)

An account of the remarkable colour changes which this substance undergoes in alkaline solution has been given in the introduction.

*7-Methyl-4-coumaryl-p-dimethylamino-phenyl
ethylene.*

This was prepared in the usual way by heating *p*-dimethyl-aminobenzaldehyde (3 grams), and 7-methyl-coumarin-acetic acid (4 grams) with piperidine for 4-5 hours at 140° - 150° . The product was purified by dissolving in dilute hydrochloric acid in the cold, and reprecipitating with ammonia. Recrystallised from alcohol or acetic acid, it came down in beautiful orange-coloured needles which melted to a dark red liquid at 190° . Its solution in mineral acids is colourless.

(Found : C=78.32; H=6.61. $C_{20}H_{19}O_2N$ requires C=78.69; H=6.23 per cent.)

A yellow crystalline *picrate* is precipitated on addition of aqueous picric acid to a hot alcoholic solution of the compound. It turned red and melted at 204° and then decomposed with a small explosion.

The following *salts* were prepared by adding the reagents to a solution of the base in dilute hydrochloric acid :—

The *mercurichloride* separated in colourless prisms which were moderately soluble in hot water.

The *dichromate* came down as a chocolate brown precipitate which decomposed on boiling with water.

The *platinichloride* formed a pale yellow precipitate.

The *ferrocyanide* was precipitated as a light green crystalline powder.

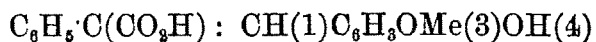
*α -naphthapyrone-4-p-dimethylaminophenyl
ethylene.*

This was prepared from the aldehyde (2.5 grams) α -naphthacoumarin acetic acid (4 grams) and piperidine by heating to 140° for a couple of hours. The product was purified as in the preceding case, and then crystallised twice from hot absolute alcohol. Deep red prisms were deposited melting at 215° - 216° . The yield was poor amounting to only 0.6 grams. (Found: C=81.30; H=5.73. $C_{23}H_{19}O_2N$ requires C=80.94; H=5.57 per cent).

The *hydrochloride* is sparingly soluble, and crystallises from hot concentrated solutions in colourless needles. On diluting the solution with water, the compound gradually dissociates into the free base which comes down as a red precipitate. (Found: Cl=10.21. $C_{23}H_{19}O_2N, HCl$ requires Cl=9.4 per cent.)

B. SUBSTITUTED STILBENES AND STILBENE
CARBOXYLIC ACIDS.

4-hydroxy-3-methoxy-stilbene- α' -carboxylic acid



Vanillin (2 grams), sodium phenyl acetate (6 grams) and acetic anhydride (15 c. c.) were boiled under reflux for six hours, and the product poured into water and boiled to decompose the excess of acetic anhydride. An oil was precipitated which, on standing overnight, completely solidified. The solid was powdered and digested for an hour with cold sodium carbonate when most of it dissolved leaving a small amount of a white residue which was found to be acetyl vanillin. The solution was acidified and the precipitate redissolved in 2N caustic soda and boiled in order to decompose the acetyl derivative simultaneously formed. On acidifying the cold solution a colourless solid was deposited which was found to be pure after one crystallisation from alcohol. It formed colourless rectangular plates sintering at 181° and melting at 186° - 87° . Its solutions in alkalis or alkali carbonates are colourless.

(Found: C=71.34; H=5.38. $\text{C}_{16}\text{H}_{14}\text{O}_4$ requires C=71.11; H=5.18 per cent.)

4-hydroxy-3-methoxy-stilbene, was the sole product isolated on heating vanillin (5.5 grams), phenyl acetic acid (5 grams) and piperidine to 140° - 150° for four hours. The solid obtained on pouring into water was washed with alcohol and sodium carbonate, and the residue crystallised twice from alcohol. Glistening leaflets melting at 134° were obtained, which slowly went into solution when treated with cold sodium hydroxide (2N). The solution had a pale yellow tint, and on dilution, exhibited a blue fluorescence. It was insoluble in sodium carbonate.

(Found: C=79.21; H=6.02. $C_{15}H_{14}O_2$ requires C=79.64; H=6.19 per cent.)

3: 4-*Dimethoxy stilbene* obtained by methylating the above compound crystallised from alcohol in soft colourless needles melting at 111°.

(Found: C=80.31; H=6.90. $C_{16}H_{16}O_2$ requires C=80.00; H=6.66 per cent.)

5-*Bromo-4-hydroxy-3-methoxy-stilbene- α' -carboxylic acid* prepared by Perkin's method from 5-bromo-vanillin (7 grams), sodium phenyl acetate (4 grams) and acetic anhydride (15 c. c.), separated from alcohol in colourless foliated crystals melting at 222°. It dissolved in cold sodium carbonate to a colourless solution.

(Found: Br=22.95. $C_{16}H_{13}O_4Br$ requires Br=22.92 per cent.)

4-hydroxy-3-methoxy-2': 4'-dinitro-stilbene.

Vanillin (5 grams), *meta*-dinitro-toluene (6 grams) and piperidine were heated to 150°-160° for two hours, and the dark melt transferred to a dish where it solidified on cooling. The solid was powdered, washed carefully with small amounts of cold alcohol, and then crystallised twice from boiling glacial acetic acid. Deep red oblong plates m.p. 193° were obtained, weighing nearly 2 grams.

(Found: C=57.41; H=3.98. $C_{15}H_{12}O_6N_2$ requires C=56.96; H=3.80 per cent.)

The substance turns black immediately on the addition of dilute alkalis and on warming, slowly goes into solution with a dark brown colour. On acidifying the solution the original red substance is reprecipitated.

p-*Dimethylamino stilbene*, prepared by heating a mixture of phenyl acetic acid (4 grams), *p*-dimethyl amino benzaldehyde (3.3 grams) and piperidine at 160° for three hours, crystallised from alcohol in colourless

broad glistening leaflets melting at 150° . The same compound appears to have been synthesised by Sachs and Sachs (Ber. 1905, 38, 51) by treating *p*-dimethylamino benzaldehyde with magnesium benzyl chloride and heating the carbinol obtained under 10 mm. pressure. It forms a sparingly soluble hydrochloride (m.p. 174°) which dissolves in a large excess of water without appreciable dissociation.

(Found: $N=6.49$. $C_{16}H_{17}N$ requires $N=6.28$ per cent.)

Methylene ether of 3:4-dihydroxy stilbene- α' -carboxylic acid.

Piperonal (4.5 grams) sodium phenyl acetate (5 grams), and acetic anhydride (12 grams) were heated to 150° - 160° for six hours. The product was poured into water, boiled, and the solid extracted with cold sodium bicarbonate and reprecipitated with acids. Crystallisation from alcohol gave colourless prisms melting at 231° - 32° . The white *silver salt* was analysed.

(Found: $Ag=28.31$. $C_{16}H_{11}O_4Ag$ requires $Ag=28.80$ per cent.)

The *ethyl ester*, prepared by treating the silver salt with ethyl iodide in dry benzene, crystallised in hard rhombic prisms melting at 104° .

(Found: $C=72.74$; $H=5.48$. $C_{18}H_{16}O_4$ requires $C=72.97$; $H=5.40$ per cent.)

Methylene ether of 3:4-dihydroxy stilbene

Phenyl acetic acid, piperonal and piperidine were heated for six hours at 170° and the product washed with cold alcohol and then digested with sodium carbonate solution when most of it dissolved. In acidifying the alkaline solution and crystallising the resulting precipitate from alcohol, colourless prisms (m.p. 232°) of the stilbene carboxylic acid were obtained. The residue which

weighed about 0.3 grams was washed with a little dilute sodium Hydroxide and then crystallised from alcohol when beautiful shining needles appeared, m.p. 95° - 96° . (Found: C=79.96; H=5.05. $C_{15}H_{12}O_2$ requires C=80.35; H=5.35 per cent.) It readily formed a *dibromide* which came down from benzene in small white crystals melting at 187° . The compound is evidently identical with the stilbene prepared by Helland Wiegandt (Ber. 1904, 37, 1431-32) by condensing benzyl magnesium chloride with piperonal and then distilling the product.

Methylene ether of 3:4-dihydroxy-2':4'-dinitrostilbene.

Piperonal (5 grams), and *meta*-dinitro-toluene (6 grams) were heated with piperidine at 150° for about two hours, and the product worked up in the usual way. Crystallised from glacial acetic acid, it came down in reddish brown plates melting at 183° .

(Found: N=9.37. $C_{15}H_{10}O_6N_2$ requires N=8.92 per cent.)

PRESIDENCY COLLEGE,

MADRAS.

(Received, Dec. 1, 1924.)

Cobalti-ammine Chromates and Chromato Cobalti-ammines.

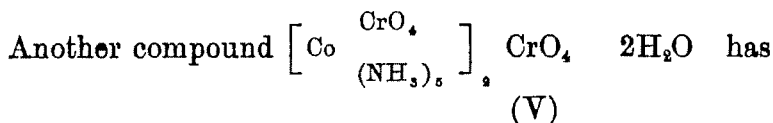
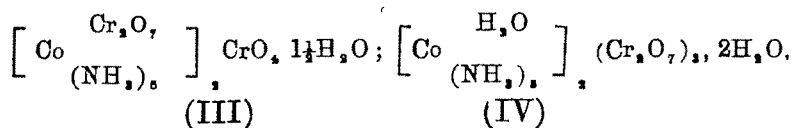
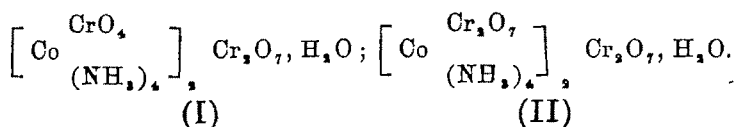
BY

PRIYADARANJAN RAY

AND

PULIN VIHARI SARKAR.

Briggs (Trans. Chem. Soc. 1919, 115, 67) has studied the action of potassium chromate and potassium dichromate on neutral aquo-tetrammine and aquo-pentammine cobaltisalts and has succeeded in isolating some chromato-cobalti-ammine compounds. In the present paper the action of chromic acid upon carbonato-tetrammine and carbonato-pentammine cobaltisalts has been described. It has been found that the course of the reaction in most cases differs entirely from that observed by Briggs and the products obtained are mostly different. The following compounds have been obtained :—



been obtained by the action of ammonium chromate and ammonia upon cobaltous hydroxide in presence of air.

Briggs has also obtained by the action of potassium chromate upon neutral aquopentammine chloride, a chromato-pentammine chloride, from which by the action of silver chromate, he prepared a chromato-pentammine chromate with three molecules of water of crystallisation.

EXPERIMENTAL.

Action of Chromic Acid on Carbonato-tetrammine Cobaltic Nitrate:—Chromato-tetrammine Cobaltic Dichromate.—

4 grs. of carbonato salt was dissolved in 60 c. c. of water and to this was slowly added with stirring a solution of 2 grms. of chromic acid in 20 c. c. of water. A dirty brown precipitate was at once produced which was washed with water, then with alcohol and dried in a desiccator over lime and calcium chloride. It could be recrystallised from hot water containing a few drops of acetic acid, yield:—3 gms.

The substance was sparingly soluble in water giving a brownish-yellow solution which on heating decomposed with the precipitation of cobaltic oxide. When heated in a dry test tube the substance ignited suddenly with explosive violence, gave out ammonia and nitrogen and a bluish green inflated mass was left behind. Solution of the substance in water gave precipitates with barium nitrate, silver nitrate and lead acetate solutions; the precipitate formed increased after addition of sodium acetate solution indicating the presence of an ionogen dichromate group in the outer zone. The solution of the substance was found acid to litmus. The filtrate obtained after precipitation with barium nitrate and sodium acetate, became slowly opaque on keeping and gave a further precipitate of barium chromate; lead acetate also precipitated yellow lead-chromate from the filtrate. These facts proved the presence of a chromate group in the inner zone. On the other hand, silver nitrate and lead

acetate when added to the solution of the substance together with sodium acetate precipitated the whole of the chromate showing that the substance was readily hydrolysed in water into a di-aquo salt.

Analysis:—

Found—Co = 16.52, 16.64 ;

CrO₃ = 56.3, 55.4 ;

and NH₃ = 19.19 per cent.

Monohydrated chromato-tetrammine-dichromate (formula I).

$[(\text{NH}_3)_4\text{CoCrO}_4]_2 \text{Cr}_2\text{O}_7, \text{H}_2\text{O}$ requires.

Co = 16.4 ; CrO₃ = 55.8 ; and NH₃ = 18.94 per cent.

The molecule of water was lost by drying in vacuum over sulphuric acid. Briggs (l. c.) also obtained a similar compound of the composition $[(\text{NH}_3)_4\text{CoCrO}_4]_2 \text{Cr}_2\text{O}_7, 2\text{H}_2\text{O}$ by the addition of a neutral diaquo-tetrammine cobaltic nitrate to a solution of potassium dichromate and by drying the product in air.

Dichromato-tetrammine Cobaltic Dichromate.

To a solution of 5 gms. of chromic acid in 20 c.c. of water, a solution of 2 gms. of carbonate salt in 40 c.c. of water was slowly added with stirring. The solution was filtered and allowed to stand overnight. A blackish crystalline deposit was obtained ; it was filtered and washed with water. From the filtrate a second crop of the substance could be obtained on further keeping. It was recrystallized from hot water containing a little chromic acid. The substance was dried in vacuo over calcium chloride and lime. Yield :—1 gm.

The substance when finely powdered was yellowish brown. It was moderately soluble in water giving a deep reddish brown solution which decomposed on heating. The solution was strongly acid to litmus. The dry substance decomposed on ignition with explosive violence giving out nitrogen and ammonia and leaving a voluminous greenish blue residue. Barium salt solutions gave only slight precipitate with the solution of the substance unless sodium acetate was added. But in the presence of sodium acetate the precipitation was immediate and complete and the filtrate was free from chromate ion. Silver nitrate and lead acetate solution behaved in the same way. It seemed, therefore, that the substance was either an aquo-compound or one which was immediately hydrolysed in solution into an aquo-compound.

Analysis:—

Found—Co = 12·84, 13·2;

Cr O₃ = 62·4, 62·4;

and NH₃ = 15·1, 15·2 per cent.

From the results of analysis the only possible formula is what agrees with No. (II) *i.e.*, dichromato-tetrammine cobalti-di chromate with one molecule of water of crystallisation. The formula for the alternative aquo-compound $[\text{Co}(\text{H}_2\text{O})_2 (\text{NH}_3)_4]_2 (\text{Cr}_2\text{O}_7)_3$ requires Co=12·1, CrO₃=61·5 and NH₃=14·0 per cent. whereas $[\text{Co}(\text{NH}_3)_4 \text{Cr}_2\text{O}_7]_2 \text{Cr}_2\text{O}_7, \text{H}_2\text{O}$ requires Co=12·82, Cr O₃=65·2, and NH₃=14·8 per cent. which is much nearer the experimental values barring that of chromium, the low value of which may be attributed to the partial hydrolytic decomposition of the product which could not be avoided even by recrystallisation in presence of chromic acid.

Action of chromic acid upon carbonato-pentammine cobaltic nitrate:—

Dichromato-pentammine Chromate.

To a solution of 4 gms. of carbonato-pentammine salt in 120 c.c. of water, a solution of 2 gms. of chromic acid in 10 c.c. of water was slowly added with stirring. A red crystalline precipitate was formed. It was then recrystallized from hot water, washed and dried in vacuo over sulphuric acid. Yield:—3.5 gms.

It formed brownish red shining silky crystals; sparingly soluble in water. Barium, lead and silver salts at once precipitated the chromate ion from the solution in the cold, the amount of precipitate increased on the addition of sodium acetate. The filtrate obtained after precipitation with barium nitrate and sodium acetate solution however became slowly turbid but rapidly on warming and gave a further precipitate of barium chromate showing that a part of the chromate ion was in the complex though loosely held. Lead acetate and silver nitrate solution precipitated the whole of the chromate ion even in the cold. The solution of the substance was acid to litmus and as the addition of sodium acetate solution increased the amount of the precipitate, dichromate groups must have been present in the substance. When heated in a dry test tube it exploded with the evolution of ammonia, nitrogen and water and a greenish residue was left behind.

Analysis:

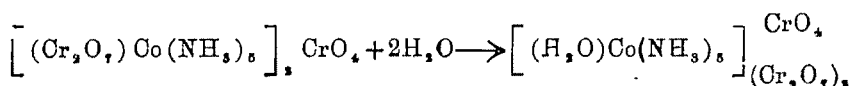
Found:— Co=13.4, 13.42;

CrO₃=57.7;

and NH₃=20.4 per cent..

Dichromato-pentammine cobaltic chromate (formula III) requires Co=13.65; CrO₃=57.7; and NH₃=19.7 per cent.

The only other possible formula agreeing with the results of analysis would be aquo-pentammine chromate dichromate but this is barred out by the fact that a part of the chromate ion is undoubtedly in the complex as whole of the chromate is not removed in the cold by barium nitrate and sodium acetate solution. But from the behaviour of the substance in solution it can be asserted that it hydrolyses very readily in water giving rise to the formation of an aquo salt as shown below :—



On the other hand an excess of chromic acid solution with carbonato-pentammine cobaltic nitrate gave rise to the formation of a brick-red crystalline precipitate which was recrystallized from hot dilute chromic acid solution.

The substance was sparingly soluble in water and acid to litmus. The whole of the chromate radical was precipitated in the cold with barium, lead and silver salt solutions in the presence of sodium acetate showing that there was no chromate radical within the complex. Hence it was only an aquo-pentammine compound.

Analysis :

Found :—Co = 11.67 ; CrO_3 = 59.3 ; and NH_3 = 17.4 per cent.

Aquo-pentammine cobaltic dichromate (Formula IV) requires Co = 11.7 ; CrO_3 = 59.4 ; and NH_3 = 17 per cent.

Action of Ammonium Dichromate and Ammonia upon Cobalt Hydroxide and the formation of Chromato-pentam-mine Cobaltic Chromate.—

Freshly precipitated and purified cobalt hydroxide from 25 gms. of cobalt nitrate was treated with 20 gms. of ammonium dichromate and 250 c.c. of concentrated

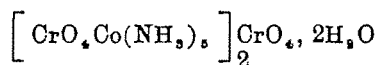
ammonia, the solution readily became dark brown and a portion remained undissolved which was filtered off on the pump. A rapid current of air was then passed through the filtrate for about 3-4 hours; and the whole was left to stand overnight. A reddish brown crystalline powder separated at the bottom next day. It was then filtered, washed with water and dried in vacuo over sulphuric acid. It was further purified by dissolving in a large volume of water and then precipitating by alcohol. The filtrate on exposure to air yielded a further crop of crystals. The yield was quite satisfactory.

The reddish brown crystals obtained in the above way were sparingly soluble in water and the solution was neutral to litmus. Barium, silver and lead salt solution removed only a part of the chromate as insoluble precipitates in the cold; the filtrate after the first precipitation on warming with a few drops of acetic acid gave a further copious precipitate of the insoluble chromates proving that a part of the chromate radical was within the complex and a part without it.

Analysis:

Found:—Co = 17.95; CrO₃ = 44.23 per cent.

Chromato pentammine chromate



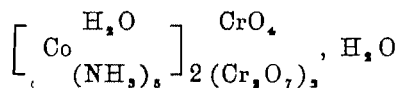
requires Co = 17.56; CrO₃ = 44.3 per cent.

The substance on heating with concentrated hydrochloric acid gave characteristic red crystals of chloropentammine chloride proving it to be a pentammine compound.

The above compound on recrystallization from dilute acetic acid gave a brick-red silky crystalline product which on examination and analysis was found to be an aquopentammine chromate dichromate,

Analysis :

Found: Co = 13.13 ; CrO₃ = 55.86 per cent.



requires Co = 13.25 ; CrO₃ = 56.1 per cent.

The residue left after the treatment of the cobalt-hydroxide with ammonia and ammonium dichromate, was extracted with water. To the solution strong ammonia was added when a yellow crystalline precipitate was produced. It was found on qualitative analysis to be identical with hexammine cobaltic chromate.

It may be mentioned in this connection that the action of iodic acid solution upon carbonato-tetrammine and carbonato-pentammine cobaltic nitrate gave rise to the formation of only the corresponding aquo-iodates.

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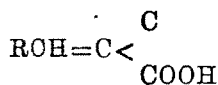
A General Synthesis of α -Unsaturated Acids from Malonic Acid.

Part I

By

SIKHIBHUSHAN DUTT.

Malonic acid has previously been condensed with aliphatic and aromatic aldehydes with the formation of alkylidene- and arylidene-malonic acids (Ann. 218, 145, 169; Stuarts, J. C. S., 1886, 365; Ann. 253, 374). (The usual condensing agents employed in these cases are invariably glacial acetic acid or acetic anhydride.) In the case of aliphatic aldehydes the corresponding dicarboxylic acids, being very unstable, generally decompose under the experimental conditions into the corresponding α -unsaturated monocarboxylic acids and carbon dioxide. But in the case of aromatic aldehydes, such decomposition is not effected and they are isolated as unsaturated dicarboxylic acids with the general constitution, of



These when heated much above their melting points, are slowly decomposed into the corresponding monocarboxylic acids with the elimination of carbon dioxide.

In the course of the following investigation it has been found that malonic acid easily condenses with aldehydes in presence of piperidine in pyridine solution to alkylidene- and arylidene-malonic acids, which under the influence of pyridine particularly on heating lose carbon dioxide with the greatest ease yielding α -unsaturated monocarboxylic acids in excellent yields. The

influence of pyridine in these cases is very interesting, as the corresponding dicarboxylic acids in their isolated conditions are not appreciably decomposed on heating to the boiling temperature of pyridine, *viz.*, 116°C. In pyridine solution, however, they get decomposed even at ordinary temperature though very slowly, and very rapidly at 100°C. The alkaline nature of pyridine has probably nothing to do in this connection as the dicarboxylic acids in caustic alkali solution do not eliminate carbon dioxide on heating, but are decomposed into the corresponding aldehydes of malonic acid.

Comparing with Perkin's method of synthesis of unsaturated acids from aldehydes, it has been found that the present method is superior to the former as it gives a much better yield of an exceedingly pure substance. The process is also much easier and quicker to carry out than Perkin's method. The only drawback of this process is that aromatic hydroxy-aldehydes either do not react or give a bad yield. This, however, can be remedied to a considerable extent by employing carbethoxy derivatives of these hydroxy-aldehydes in place of the parent substances. Even then the yield of the unsaturated acid^o is not quite so good as that obtained with non-hydroxy-aldehydes in this process.

It has been found that ketones also react with malonic acid by this process. Except in the case of acetone the yield of the corresponding unsaturated acid obtained is, however, far from satisfactory.

EXPERIMENTAL.

Condensation with Aldehydes and Ketones.

General Procedure.

The aldehydes and ketones mentioned below were mixed with suitable quantities of malonic acid and pyridine and a few drops of piperidine and heated under

reflux for periods varying between one to six hours, except in the case of cinnamic aldehyde which required sixteen hours. After reaction the mixtures were poured into water and acidified with hydrochloric acid, when the products separated out as crystals. These were further purified by crystallisation and identified. In some cases, as mentioned below, the products were extracted, from the acidified aqueous mixture, with ether and crystallised from these ethereal solutions.

Condensation with Aldehydes.

(1) *Acetaldehyde*.—The product was extracted with ether and the ethereal layer was shaken with sodium carbonate solution, and the aqueous solution separated. Crystals which separated on evaporating the ethereal solution melted at 72°C. Yield 75%. Identified to be crotonic acid.

(2) *Glyoxalic acid*.—The product crystallised from hot water. Sublimes at 200° without melting. Identified to be fumaric acid. Yield 1.8 gms. from a mixture of 10 gms. of glyoxalic acid and 10 gms. of malonic acid.

The filtrate after separating the above product from aqueous solution was shaken with ether. Long crystals were obtained from this solution by evaporation. M. P. 130°C. Identified to be maleic acid, yield 2.8 gms.

(3) *Benzaldehyde*.—Product crystallised from hot water was identified to be cinnamic acid. M. P. 133°C. Yield 90%.

(4) *p-Toluic Aldehyde*.—Product crystallised from dilute acetic acid was identified to be *p*-methyl cinnamic acid (Ber. 23, 1033) M. P. 198°C. Yield 87%.

(5) *Furfurol*.—Product which crystallised from hot water was identified to be furfuralacrylic acid. M. P. 140°C. Yield 70%.

(6) *o*-Nitrobenzaldehyde.—Product crystallised from glacial acetic acid. Identified to be *o*-nitrocinnamic acid. M. P. 236°. Yield 73%.

(7) *m*-Nitrobenzaldehyde.—Product crystallised from glacial acetic acid. Identified to be *m*-nitrocinnamic acid. M. P. 196°. Yield 90%.

(8) *p*-Nitrobenzaldehyde.—Product crystallised from glacial acetic acid. Identified as *p*-nitrocinnamic acid. M. P. 285°. Yield 82%.

(9) *Piperonal*.—Product crystallised from glacial acetic acid. Identified as piperonyl acrylic acid (J. C. S., 1891, 59, 153). M. P. 232°C. Yield 76%.

(10) *Anisaldehyde*.—Crystallised from alcohol. Identified to be *p*-methoxycinnamic acid. M. P. 172°C. Yield 80%.

(11) *p*-Dimethylaminobenzaldehyde.—The product was poured into water and acidified with acetic acid. Product was finally crystallised from alcohol. Identified as *p*-dimethylaminocinnamic acid. M. P. 216° (Monat. 29, 899). Yield 65%.

Found: N=7.1. $C_{11}H_{13}NO_2$ requires N=7.3%.

(12) *m*-Bromobenzaldehyde.—Product was crystallised from glacial acetic acid and identified to be *m*-bromocinnamic acid. M. P. 178°C. Yield 83%.

(13) *Salicylaldehyde*.—The product after acidification with HCl in water was steam-distilled to remove excess of salicylaldehyde. Product crystallised out from mother-liquor on cooling and was identified to be *o*-coumaric acid. M. P. 200°C. Coumarin was obtained on treating this with 85% sulphuric acid. Yield of coumaric acid 20%.

(14) *Vanillin*.—(Carbethoxyvanillin was used.) Precipitate was extracted with sodium carbonate solution and acidified. The precipitate thus obtained was dissolved in alcohol and crystallised by evaporation. Identified to be ferulic acid. M. P. 168°C. Yield 12%.

(15) *Protocatechuic Aldehyde*.—(Dicarbethoxy derivative was used.) Crystallised from alcohol. Identified as caffeic acid. M. P. 213°C . Yield 7%.

(16) *Cinnamic Aldehyde*.—Crystallised from acetic acid and identified to be cinnamylidene acetic acid (Perkin, J. C. S. 1877, 1, 403). M. P. 165°C . Yield 60%. If heated only for two hours the main product is cinnamylidene malonic acid (Stuart, J. C. S. 1886, 365). M. P. 208°C . Yield 70%. On boiling in pyridine solution the transformation to cinnamylidene acetic acid is quantitative.

Condensation with Ketones.—In the following cases the reaction mixture was allowed to stand at ordinary temperature for 24 hours and then heated for two hours. The ethereal extract from water was treated with sodium carbonate solution, separated from aqueous layer, treated with a little animal charcoal, filtered, dried and evaporated.

(1) *Acetone*.—Product identified to be $\beta\beta$ -dimethylacrylic acid. M. P. 69°C . Yield 60%.

(2) *Diethylketone*.—Product was a thick oil which distilled at 218° – 220°C . Identified to be $\beta\beta$ -diethylacrylic acid. (Ber. 1. 519). Yield 35%.

(3) *Cyclohexanone*.—Product identified to be *Cyclohexylidene acetic acid* (Wallach, Ann., 353, 888). Yield rather bad, not exceeding 5% even under most favourable conditions.

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The Condensations of Chloroform, Carbon-tetrachloride and Iodoform with Resorcinol and similar other Hydroxy Aromatic Compounds.

By

RAJENDRA NATH SEN,

NRIPENDRA NATH SINHA AND NRIPENDRA NATH SARKAR.

Chloroform and carbontetrachloride have been previously employed in the synthesis of triphenylmethane and some of its derivatives. (Friedel and Craft, *Compt. rend.* 1877, 84, 1453; O. Fisher, *Annalen* 1879, 194, 254; Gomberg, *Ber.*, 1900, 33, 3144; Haumann D.R.P. 68976; *Frđl.* III. 103; *Ann. Chim. Phys.* VI. 1, 489.) In all these cases Friedel and Crafts' method or a modification of it was employed, AlCl_3 or ZnCl_2 being used as a condensing agent. In the year 1858 Hofmann observed that aniline when heated with carbontetrachloride yielded *p*-fuchsin, and this method was used on a manufacturing scale by Monnet and Dury in Lyons. A fair yield of *p*-fuchsin hydroiodide was also obtained by simply heating iodoform with pure aniline. Dyes of the aurin type have been recently obtained by H. Baines and J. E. Driver by heating dry sodium and potassium salts of phenol and cresols in the vapour of chloroform and carbon tetrachloride. (*J. Chem. Soc.*, 1923, 123, 1214; *J. Chem. Soc.*, 1924, 125, 907, 910.)

The present investigation was undertaken with a view to determine whether compounds of the type of benzeins can be obtained by the condensation of chloroform, carbontetrachloride and iodoform with resorcin and other hydroxy aromatic compounds.

Excess of pure and dry chloroform or carbontetrachloride was dropped through a long reflux condenser into molten resorcin or other hydroxy compound at a temperature of 140° to 160°C . Powdered anhydrous zinc chloride was then added to the mass and the mixture was heated to a temp. of 180° to 200°C for 3 to 4 hours when the reaction was complete. The product when purified and analysed was found to be a benzein.

In the case of condensation with chloroform the leuco condensation-product is apparently oxidised by air to the carbinol stage.

The condensations of iodoform with resorcin and other hydroxy aromatic compounds have been effected by heating a mixture of the components in requisite proportions at 160° to 180°C ., with or without the addition of anhydrous zinc chloride.

Identical product, *viz.*, resorcin-*o-p*-dihydroxy-benzein, has also been prepared by Sen and Sarkar by condensing *o-p*-dihydroxy benzyl alcohol with resorcin in the presence of conc. sulphuric acid of sp. gr. 1.84. (To be shortly published.) The products of the condensation of pyrogallol with chloroform and iodoform are identical and non-fluorescent. The condensation product of hydroquinone and iodoform exhibits weak blue fluorescence in alkaline solution but in dilute alcoholic solution it shows a marked green fluorescence.

EXPERIMENTAL.

(1). *Chloroform and Resorcin*.:—5 gms. of dried resorcin were melted in a wide-mouthed flask provided with a long reflux condenser. 5 to 6 c.c. of extra pure chloroform were added drop by drop to the molten mass in the course of 15 minutes. Immediately reddish brown colour developed. Fused zinc chloride (2 gms.) was added and

the temp. was raised to 180° to 200°C. Hydrochloric acid was evolved (detected by ammonia) and the reaction was complete in 3 to 4 hours. Excess of chloroform was driven off and the product was washed with hot water acidified with hydrochloric acid. It was then dissolved in dil. sodium hydroxide solution and the alkaline solution was filtered. From the filtrate the original compound was precipitated by dil. hydrochloric acid. The precipitate was thoroughly washed with hot water containing hydrochloric acid and finally purified from rectified spirit when an orange yellow micro-crystalline powder was obtained. Yield 4 gms. It does not melt below 290°C. It dissolves in alkali with red colour and green fluorescence. It is soluble in alcohol and acetone (green fluorescence), but insoluble in benzene and ether. It dyes wool and silk an orange shade. (Found: C=71.10% and H=3.79%; Resorcin-*o-p*-dihydroxy-benzein, $C_{12}H_{10}O_2$ requires C=71.25% and H=3.75%). On bromination it gave a tetra-bromo compound like eosin which dyes wool and silk a red shade. (Found: Br=50.11%. Tetra-bromo resorcin-*o-p*-dihydroxy-benzein, $C_{12}H_6O_2Br_4$ requires Br=50.3%).

(2) *Chloroform and Pyrogallol*.—3.75 gms. of pyrogallol and 4 c.c. of chloroform were heated with 2 gms. of fused zinc chloride as in expt. (1), for 3 to 4 hours. Similar method of purification was adopted as in expt. (1). A black product was obtained which does not melt below 250°C. It dissolves in alkali without any fluorescence. It is soluble in alcohol, sparingly so in acetone, but insoluble in benzene and ether. (Found: C=61.82% and H=3.38%. Pyrogallol-*o-m-p*-trihydroxy benzein, $C_{12}H_{12}O_3$ requires C=61.95% and H=3.26%).

(3) *Iodoform and Resorcinol*.—3.5 gms. of resorcin and 4 gms. of iodoform were intimately mixed together and the mixture was heated at a temp. of 160°-180°C

for 3 to 4 hours. Processes of purification as in expt. (1). (Found: C=71.04% and H=3.85%. Resorcin-*o-p*-dihydroxy benzein, $C_{19}H_{12}O_6$ requires C=71.25% and H=3.75%).

(4) *Iodoform and Pyrogallol*.—3.75 gms. of pyrogallol and 3.9 gm. iodoform were mixed together and the mixture was heated to a temp. of 160° to 180°C. It was purified as before. (Found: C=61.75% and H=3.46%. Pyrogallol-*o-m-p*-trihydroxy benzein, $C_{19}H_{12}O_8$ requires C=61.95% and H=3.26%.)

(5) *Iodoform and Hydroquinone*.—3.5 gms. of hydroquinone and 3.9 gms. of iodoform were treated exactly in the same way in which iodoform and resorcin were treated. The purification of the condensation product was exactly similar as in previous experiments. Hydroquinone-*o-m'*-dihydroxy benzein thus obtained does not melt below 250°C. It dissolves in alkali with red colour and faint blue fluorescence. It is very soluble in alcohol and acetone (green fluorescence) but insoluble in ether and benzene. (Found: C=70.95% and H=3.9%. Hydroquinone-*o-m'*-dihydroxy benzein, $C_{19}H_{12}O_6$ requires C=71.25% and H=3.75%.)

(6) *Carbontetrachloride and Resorcinol*.—5 gms. of resorcin were treated with 6 to 7 c.c. of carbontetrachloride precisely in the same manner as in expt. (1). The condensation product has identical properties as of the product obtained in expt. (1). (Found: C=71.1% and H=3.64%. Resorcin-*o-p*-dihydroxy benzein, $C_{19}H_{12}O_6$ requires C=71.25% and H=3.75%.)

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[Received, February 14, 1925.]

Equilibrium of the Ternary System Bismuth Oxide, Hydrochloric Acid and Water.

BY

GHULAM WARIS.

Various hydrates of bismuth oxychloride have been described in the literature. Heintz [Pogg. Ann. 63, 55 (1884)] states that the precipitate first obtained by the addition of water to a solution of bismuth chloride containing hydrochloric acid is a monohydrate of bismuth oxychloride, which on keeping in a desiccator passes into the anhydrous oxychloride.

Phillips (Berz. Jahrsber. 11, 187) believes in the existence of a trihydrate of bismuth oxychloride, which he describes as occurring in tetragonal crystals.

Schulten [Bull. Soc. Chim. (3), 23, 156, 1906] describes a bihydrate of bismuth oxychloride.

The object of this paper is to account for divergence of opinion amongst different workers.

PREPARATION OF MATERIALS.

Bismuth Trioxide.—Bismuth trioxide was obtained by heating strongly crystals of bismuth nitrate carefully prepared.

Bismuth Trichloride.—Commercially pure bismuth trichloride was heated in a tube of the shape used by Faraday for liquefaction of gases, and the moisture sucked out by exhausting to 1 or 2 cm. pressure, while the bismuth trichloride was being heated. Then the open end of the tube was sealed. On heating more strongly bismuth trichloride partly distilled into the other arm as a yellow liquid and partly sublimed in white

crystals. The substance was kept in the sealed tube till required for use.

EXPERIMENTAL.

The solubility tubes were made by blowing an elongated bulb in the middle of a glass tube of 1 cm. bore and sealed at one end. The relative size of the bulb and its lower part was such that the solid phase separating out at the ordinary temperature could be contained in two-thirds of the lower tubular portion, and about one-third of the bulb was kept empty in order to ensure free mixing.

After filling and sealing the tubes, they were placed in a thermostat electrically maintained at 25°.

Equilibrium was attained in about 12 hours' shaking and after having allowed the solid phase to settle down, the tube was opened and the contents analysed.

METHOD OF ANALYSIS.

The clear liquid was sucked off with a small bulb-tube provided with a rubber tubing and a pinch-cock. It was weighed and dissolved in 1:1 sulphuric acid, and the solution made up to 50 c.c. When the bismuth content was great it was necessary to use somewhat stronger acid (2:1).

The composition of the solid phase was determined by Schreinmaker's method of residues.

Bismuth was precipitated as sulphide by passing H_2S to saturation in the dilute solution. The precipitate was filtered off, washed free of hydrochloric acid. The precipitate was dissolved in hot nitric acid and the ordinary process of precipitating with excess of ammonium carbonate, igniting the basic carbonate and weighing as Bi_2O_3 , was followed. The results obtained by this method were found correct to within 0.03%.

Chlorine was estimated by Volhard's method as modified by Rothmund and Burgstaller [Zeit. anorg. Chem., 63, 330 (1909)].

Varying amounts of sulphuric acid did not affect the results obtained in the estimation of chlorine as duplicate observations showed a difference in the third place of decimal.

The quadruple point was investigated by partially filling a solubility tube with a saturated solution of bismuth trichloride in hydrochloric acid; some solid trichloride was then introduced, and diluted with a few drops of water till the solution was just opalescent. When equilibrium was attained, the heterogeneous solid phase, when seen under the microscope, was found to contain BiCl_3 crystals disseminated with an amorphous granular ppt.

EXPERIMENTAL RESULTS

	Percentage Composition of Liquid Phase.		Percentage Composition of Solid Phase.		Nature of Solid Phase.
	Bi_2O_3	HCl.	Bi_2O_3	HCl.	
1	0.6%	2.50%	12.05%	4.05%	BiOCl .
2	2.60%	4.22%	19.40%	6.17%	"
3	11.44%	10.68%	26.26%	11.60%	"
4	13.16%	12.00%	25.40%	12.32%	"
5	16.41%	13.43%	27.53%	13.59%	"
6	23.75%	17.56%	31.80%	17.30%	"
7	26.42%	18.47%	28.63%	18.33%	"
8	50.74%	30.23%	53.41%	29.20%	
9	58.72%	33.67%	Not analysed.		BiCl_3
10	58.70%	34.08%	"	"	
11	58.59%	35.14%	62.04%	35.19%	,

CONCLUSION.

The results have been plotted in Roozeboom's triangle. From the tie lines it is manifest that they all intersect in the vicinity of one and only one point whose composition is given by $\text{Bi}_2\text{O}_3=89.2\%$, $\text{HCl}=13.8\%$, $\text{H}_2\text{O}=3.0\%$. By calculation the empirical formula of this compound is found to be $\text{Bi}_2\text{O}_3, 2\text{HCl}, \text{H}_2\text{O}$ or BiOCl . Thus it is evident that between the concentrations 25% and 33.67% of HCl , at 25°C , the only solid phase separating out consists of normal bismuth oxychloride. This is further confirmed by the non-existence of a break in the smooth isothermal curve joining the liquid points. This investigation shows that no hydrate of bismuth oxychloride exists, at least at the temperature of 25° .

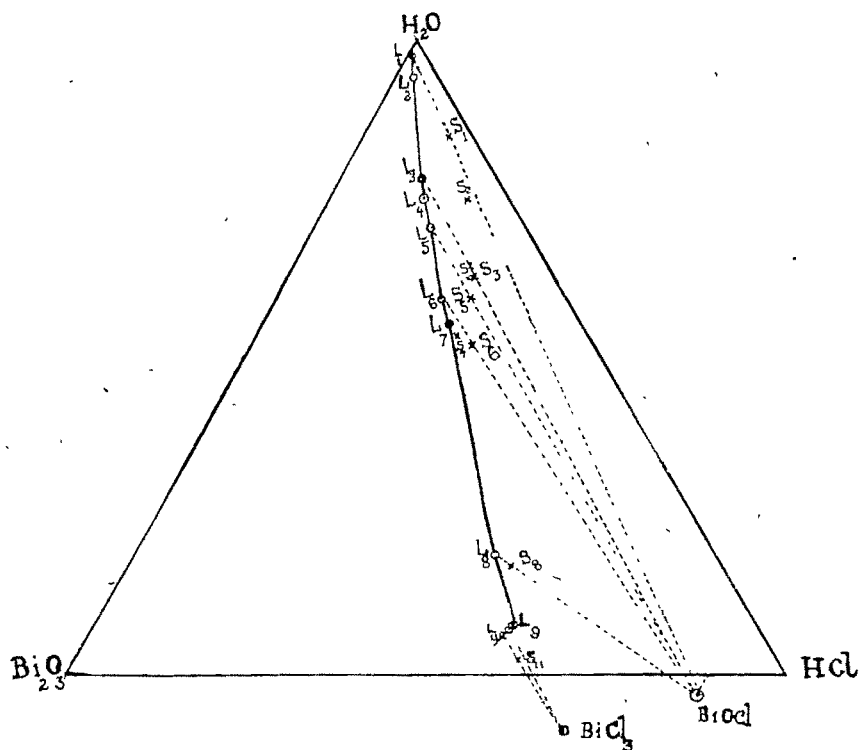
In the end the author wishes to express his sincerest thanks to Prof. B. H. Wilsdon, M.A. (Oxon.), I.E.S., for valuable suggestions while the research was being carried under his guidance as a thesis for the M.Sc. degree.

CHEMICAL LABORATORY,

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[Received, February 9, 1925.]



ISOTHERM at 25°C.

Halogenation XII.¹ Derivatives of Carbamic Esters. Chlorine as a Simultaneous Oxidising and Chlorinating Agent.

Part II.

BY

RASIK LAL DATTA

AND

BIBHU CHARAN CHATTERJEE.

It has been shewn² in a previous communication that urethanes condense with alcohols under the action of chlorine to form diurethanes, the alcohol being oxidised to the corresponding aldehyde. In the present paper, further cases have been studied.

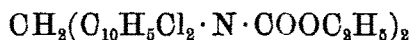
*iso*Propylurethane condenses with methyl alcohol under the influence of chlorine to form methylene dicarbamic*iso*propyl ester, $\text{CH}_3(\text{NH}.\text{COOC}_3\text{H}_7)_2$. In the case of condensation of the different urethanes with benzyl alcohol a peculiar behaviour is noticed. With aliphatic urethanes the benzyl radical remains intact while in the case of heavily substituted urethanes such as phenyl- and naphthyl-urethanes, the phenyl group is detached and the methylene radical forms the diurethanes. Methyl urethane, *n*-propyl urthane, *iso*propyl urethane, *isobutyl* urethane give rise to benzyldiene dimethylurethane, $\text{C}_6\text{H}_5\text{CH}(\text{NHCOOCH}_3)_2$, benzyldiene di-*n*-propyl urethane, $\text{C}_6\text{H}_5\text{CH}(\text{NHCOOC}_3\text{H}_7)_2$, benzyldiene

¹ Previous communications on the subject, Trans. Chem. Soc., 101 (1912), 166; J. Amer. Chem. Soc., 34 (1912), 1613; 35 (1913), 1044, 1183; 36 (1914) 389, 1007, 1011, 1014; 37 (1915), 567, 569, 578; 38 (1916), 1079, 1809, 1813, 2339, 2546; 39 (1917); 435, 441, 41 (1919), 287, 292, 2028; 43 (1921), 303; 44 (1922), 1588; 45 (1923), 480.

² Datta and Chatterjee, J. Amer. Soc., 44 (1922), 1538.

diisopropyl urethane, $C_6H_5CH(NHCOOC_3H_7)_2$ and benzylidene diisobutyl urethane, $C_6H_5CH(NHCOOC_4H_9)_2$ respectively.

By the action of chlorine on benzyl alcoholic solutions of phenyl- and naphthyl-urethanes, methylene di-*p*-chlorodiphenyl-diurethane, $CH_2(C_6H_4ClNOOC_2H_5)_2$ and methylene di-tetrachloro- α -naphthyl-diurethane,



respectively are produced, the phenyl radical being detached in both the cases. The same products are formed by the action of chlorine on methyl alcoholic solutions of the respective urethanes.¹

EXPERIMENTAL.

Action of Chlorine on isoPropyl Urethane in Methyl Alcoholic Solution. Methylenedicarbamic isopropyl Ester, $CH_2 \cdot (NH \cdot CHOOC_3H_7)_2$.

5 grams. of isopropyl urethane are dissolved in 8 c.c. of methyl alcohol and chlorinated for some time when a white solid makes its appearance. During the process the solution becomes hot and white fumes are evolved. The product on evaporation on the water-bath deposits a white solid. This is freed from adhering mother-liquor by suction, recrystallised from dilute alcohol and obtained as white silky needles melting at 110°.

Found: N=13.07. $C_9H_{18}O_4N_2$ requires N=12.84 per cent.

Action of Chlorine on Methyl Urethane in Benzyl Alcoholic Solution. Benzylidenedimethylurethane, $CH_5CH \cdot (NHCOOCH_3)_2$

5 grms. of methyl urethane are added to 8 grms. of benzyl alcohol and chloroform is added till a complete

¹ loc. cit.

solution is obtained. A current of chlorine is passed for about half-an-hour when the solution turns yellow and white fumes are evolved with the formation of white granular particles. The solution is next poured in a crystallising dish, cooled in a freezing mixture and placed in vacuum desiccator when the whole thing solidifies. The solid is freed from adhering mother-liquor by suction and pressing on the porous plate, recrystallised from benzene and obtained as white needle-shaped light crystals melting at 175° .

Found: $N=12.14$. $C_{11}H_{14}O_4N_2$ requires 11.76 per cent.

Benzylidene-di-n-propyl-urethane, $C_6H_5CH(NHCOOC_3H_7)_2$ melting at 146.7° (Found: $N=9.99$. $C_{15}H_{23}O_4N_2$ requires $N=9.52$ per cent.) *Benzylidene-di-iso-propyl-urethane*, $C_6H_5CH(NHCOOC_3H_7)_2$ melting at 148° (Found: $N=9.52$ per cent.) and *Benzylidene-di-isobutyl-urethane*, $C_6H_5CH(NHCOOC_4H_9)_2$ (Found: $N=8.89$. $C_{17}H_{25}O_4N_2$ requires $N=8.7$ per cent.) were obtained in a similar way from dipropyl-urethane, di-isopropyl-urethane and di-isobutyl-urethane respectively when dissolved in benzyl alcohol and chloroform and treated with chlorine.

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[Received, February 7, 1925.]

Vasicine—An Alkaloid Present in *Adhatoda Vasica*, Nees.

BY

JATINDRA NATH SEN

AND

TARAK PRASAD GHOSE

In the course of an investigation into the reasons for the immunity of timbers from insect and fungoid attacks which is at present being carried on at the Forest Research Institute, the active principle of *arusa* or *bakas* (*Adhatoda Vasica*, Nees) is being studied.

Some work had been done on this subject by previous workers.¹ In 1888 Hooper showed that the plant contained a white crystalline alkaloid of which he studied some properties such as the solubility and response to some of the alkaloidal reagents. Some salts were also prepared when a solution of the sulphate was found to possess a slight right-handed rotation. Bamber also studied the question and attributed the active principle to a volatile alkaloid, while Giacosa in 1895 was unable to detect any alkaloid in a sample which he examined. Hooper therefore re-examined further samples when he again found that they contained an alkaloid which he named *vasicine*. Boorsma in 1897 also demonstrated the presence of a solid alkaloid. He amplified Hooper's work and determined the melting point, which he found to be above 160°.

¹ Hooper, *Pharmaceutical Journal*, 7th April, 1888, quoted by Dymock, Warden and Hooper, "*Pharmacographia Indica*," Vol. III, pp. 50 *et seq.* Hooper, "*Adhatoda Vasica*" *Handbooks of Commercial Products, Imperial Institute Series, Indian Section*, No. 10, (1897).

Hooper's results have further been confirmed by the present investigation at Dehra Dun, when a white crystalline alkaloid has been isolated. An alcoholic extract of the dried leaves was concentrated under reduced pressure till most of the alcohol had distilled off. Warm water was then added and the aqueous solution precipitated with the help of lead acetate. Excess of lead was removed from the filtrate with the help of sulphuretted hydrogen. After getting rid of the excess of sulphuretted hydrogen, ammonia was added and the alkaloid extracted with the aid of chloroform. On evaporating off the solvent, the crude alkaloid was left in the form of a brownish solid. This was purified by repeated crystallisation from a mixture of alcohol and ether.

Estimation of vasicine was carried out in the following manner. 10 gm. of the powdered leaves were thoroughly moistened with 2 c.c. ammonia and 3 c.c. chloroform. They were then put in a percolator with 30 c.c. of ammoniated chloroform (2 c.c. ammonia per 100 c.c.) The solution was taken off at the end of 2 hours and percolation repeated with fresh additions of about 20 c.c. ammoniated chloroform till the combined extract was about 100 c.c. This was then successively shaken out with 10 c.c., 5 c.c., and 2 c.c. normal sulphuric acid diluted with two to three times its volume of water. The acid extract was treated with ammonia and treated first with 15 c.c. and then with three additions of 10 c.c. of chloroform. The solid residue left from the evaporation of the chloroform extract was then titrated with standard acid, using litmus as indicator.

The alkaloid content which varied with the season was about .2 to .4 per cent. in the samples examined.

Vasicine.—The base crystallised in the form of needles, and melted (with decomposition) at 190°-191°C.

It did not lose weight when kept in vacuo over sulphuric acid for two days. When it was dried at 100°C, the substance became slightly discoloured but no water was given off. It dissolved with ease in chloroform, alcohol, methyl alcohol and acetone, and was only sparingly soluble in water, ether, and benzene. It was practically insoluble in petrol. Treatment with strong sulphuric, nitric and hydrochloric acids or with Erdmann's (sulphuric acid containing a trace of nitric acid), Buckingham's (sulphuric acid containing ammonium molybdate) and Marquis' (sulphuric acid containing formaldehyde) reagents did not produce any characteristic colour. Solutions of salts of the base yielded characteristic precipitates with the alkaloidal reagents. Mayer's reagent (mercury potassium iodide) produced a white curd which changed into a crystalline precipitate. Sonnenschein's reagent (phosphomolybdic acid) and Scheibler's reagent (phosphotungstic acid) also produced precipitates. Characteristic double chlorides with gold and with platinum were yielded. It formed an insoluble picrolonate and a picrate the latter crystallising as needles melting at 199° (with decomposition). Mercuric chloride yielded a white precipitate. Wagner's reagent (iodine in potassium iodide) produced a red precipitate.

Combustion analyses showed that the base possesses the empirical formula of $C_{11}H_{12}N_2O$. (Found: C=70.1; H=6.5; N=14.7. $C_{11}H_{12}N_2O$ requires C=70.2; H=6.4; N=14.9 per cent).

The equivalent weight was found on titration to be 188. Vasicine forms a series of salts in which it behaves as a monacid base.

The molecular weight of the substance was determined by noting the rise in boiling point of alcohol and of benzene. (M.W.=163.2 in alcohol and 214 in benzene. $C_{11}H_{12}N_2O$ requires M.W.=188)

The base dissolved in chloroform or in alcohol was optically inactive. A solution of its sulphate was also found to be without any action on polarised light.

There does not seem to be any methoxyl group in it as negative results were obtained when it was examined by Perkin's modification of Zeisel's method, both with and without the addition of acetic anhydride.

Vasicine hydrochloride. The hydrochloride was prepared by passing hydrochloric acid gas to saturation into an alcoholic solution of the base, and then precipitating the salt with ether. Fine white needles were obtained on crystallising it from alcohol and ether. The crystals contained two molecules of water of crystallisation which were given up at 110° leaving the anhydrous salt which melted at 204° C. The salt was very soluble in alcohol and in water, sparingly so in ether. (Found: Cl=15.8. $C_{11}H_{12}N_2O$, HCl requires Cl=15.8 per cent).

Double Chloride of Vasicine and Gold. This came out as a curdy precipitate on adding gold chloride solution to an acidulated solution of vasicine chloride. On keeping rosettes of orange brown feathery plates were obtained. Purification was effected by crystallisation from acidulated water. The crystals were anhydrous as they did not lose any weight on being heated to 110° C and possessed the formula $BHAuCl_4$ (Found: Au=37.0; Cl=26.5. $C_{11}H_{12}N_2O$, $HAuCl_4$ requires Au=37.3; Cl=26.9 per cent).

Double Chloride of Vasicine and Platinum. This was prepared and purified in a similar way to the above. The crystals which were in the form of yellowish brown needles possessed the formula $B_2H_2PtCl_6$ (Found: Pt=24.2; Cl=26.6. $(C_{11}H_{12}N_2O)_2H_2PtCl_6$ requires Pt=24.8; Cl=27.1 per cent.).

Vasicine hydriodide. This salt is prepared by the addition of hydriodic acid to a suspension of vasicine in methyl alcohol. The crystals which came out on concentration were slightly yellow. Recrystallized from water they came out in fine white needles containing 2 molecules of water, but from dry methyl alcohol anhydrous crystals in the form of white needles were obtained which melted at 195°C . (Found: $\text{I}=40.0$ $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$, HI requires $\text{I}=40.2$ per cent.)

Vasicine sulphate. Similarly on adding dilute sulphuric acid to a suspension of vasicine in water and concentrating the solution, needles of vasicine sulphate came out. Recrystallised from water it contains two molecules of water of crystallisation. (In the anhydrous salt. Found: $\text{SO}_4=20.1$. $(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_2\cdot\text{H}_2\text{SO}_4$ requires $\text{SO}_4=20.5$ per cent.)

Vasicine methiodide. Vasicine dissolved in methyl alcohol was heated on water-bath with excess of methyl iodide under reflux condenser for two hours and a half. The methiodide which came out on cooling was recrystallised from methyl alcohol. The white needles thus obtained contained no water of crystallisation, and melted at 187°C . (Found: $\text{I}=38.4$. $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}\cdot\text{CH}_3\text{I}$ requires $\text{I}=38.5$ per cent).

Hydroxymethyl vasicine. Vasicine methiodide was treated with a slight excess of baryta water on the water-bath for $1\frac{1}{2}$ hours. The base which partially separated out on cooling was repeatedly extracted with hot benzene. The extract was washed with a solution of sodium carbonate and finally dried with anhydrous sodium carbonate. The substance which crystallised out on concentration was purified by recrystallisation from a mixture of benzene and petroleum ether. The prismatic crystals thus obtained were slightly brown in colour and melted at 100°C . Dried carefully at 100°C for three

hours they did not lose any weight. (Found: C=65.7; H=7.4; N=13.0. $C_{12}H_{16}N_2O_2$ requires C=65.5; H=7.3; N=12.7 per cent.).

The writers express their thanks to Mr. W. F. Perree, O.I.E., for suggesting this work, which is being further continued. They further acknowledge the help which was rendered by Mr. M. Gopal Rau, M.A., during the preliminary part of this investigation.

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Dyes derived from Phenanthraquinone.

Part VI.

Phenanthraquinone-phenyl azo-methines and Phenanthraphenazine-azo-dyes

BY

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AND

BENOY KUMAR SEN GUPTA.

In continuation of the work of Watson and Dutta, (J. C. S., T. 1921, 119, 1211), Sircar and Dutta (J. C. S., T. 1922, 121, 1944), Sircar and Sircar (J. C. S., T. 1923, 123, 1559), Sircar and Roy (J. C. S., T. 1924, 125, 543), and Sircar and Dutt (J. I. C. S., 1924, 1, 201) the present investigation was undertaken with the object of making further attempts to prepare dyes from phenanthraquinone and its substituted derivatives.

Watson and Dutta (*loc. cit.*) prepared aminophenanthraphenazines in the hope that such compounds would be quinonoid in all possible tautomeric forms, would have long chains of conjugate linkings in their molecules, and would therefore be deep coloured dyes. (*cf.* Watson, J. C. S., T. 1914, 105, 759). But they were found to be all yellow. From these observations and from the difference in the colours of the aminophenanthraphenazines from those of the corresponding azonium compounds (Dutta, J. C. S., T. 1922, 121, 1952), one is naturally inclined towards the view that the amino-azine derivatives do not exist as outlined by Watson and Dutta (*loc. cit.*) in quinonoid tautomeric forms.

It has been shown that in an azonium compound like safranin both the amino groups cannot be diazotised at

the sametime in solution of acids of moderate strengths (*cf.* Jaubert, Ber., 28, 518, 1584, etc.), and this difference in the property of the amino groups in safranine is brought forward as an argument in favour of the view that in such a compound one of the amino groups only exists as such,—the other taking part in the formation of quinonoid structure. It was therefore thought that if 2:7-diaminophenanthra-phenazine was actually a tautomeric compound, as expected by Watson and Dutta, then both the amino groups, contained in it, would not be equally easily diazotisable. With the object of testing this, attempt was made to diazotise only one amino group of 2:7-diaminophenanthraphenazine. It was further thought that if mono-azo derivatives could be prepared from 2:7-diaminophenanthraphenazine, such bodies would possess well-developed and interesting tinctorial properties like those of the mono-azo compounds obtained from safranine (*e.g.*, diazine green, diazine blue and diazine black. Ger. Pat., 95, 668, etc.).

It has now been found that, contrary to expectation, both the amino groups in 2:7-diaminophenanthraphenazine are equally easily diazotisable. On taking only half the calculated quantity of sodium nitrite, half the molecules of the 2:7-diamino-azine taken were completely diazotised, the other half remaining unchanged. Evidently, in a compound like 2:7-diaminophenanthraphenazine, no distinction can be made between the two amino groups, and this goes to prove that the molecules of the amino-azines are not in quinonoid tautomeric state like the molecules of the corresponding azonium compounds.

The bis-azo derivatives obtained from 2:7-diaminophenanthraphenazine do not exhibit the same depth of colour as the mono-azo derivatives from safranine do.

The group —N=CH— when joined to the aromatic nuclei behaves as a chromophore like the —N=N— .

(i.e., azo) linking, and a number of azo-methine dyes possessing fairly developed tinctorial properties are known (*cf.* Green and Sen, J. C. S., T. 1910, 97, 2242; Morgan and Reeves, J. C. S., T. 1922, 121, 1). It was therefore thought that if azo-methine derivatives could be prepared from the aminophenanthraquinones by condensing them with various aldehydes, such bodies might also possess interesting tinctorial properties. With that object in view 2-amino-, 4-amino-, 2:7-diamino-, and 4:5-diamino-phenanthraquinones have been condensed with one or more of the following:—benzaldehyde, *p*-tolyl-aldehyde, cinnamic aldehyde, anisic aldehyde, salicylic aldehyde, resorcylic aldehyde, dimethyl-*para*-amino-benzaldehyde, *m*-nitro-benzaldehyde, bromo-salicylic aldehyde, *para*-chlorobenzaldehyde and vanillin.

The phenanthraquinone-phenyl-azo-methines are easily obtained in well-defined crystalline forms and most of them are fairly deep coloured, but they are not satisfactory so far as their dyeing properties are concerned. They possess no affinity for cotton and are decomposed into the original amino-quinone and the aldehyde when boiled for some time with water in presence of an acid. In attempting to dye wool with these bodies from a bath containing one per cent. sulphuric acid (calculated on the weight of the wool), it was found that in every case they decomposed at the temperature of boiling water, and the colours of the dyeings obtained were invariably those of the aminophenanthraquinones. Wool can, however, be dyed with them from an one per cent. acetic acid bath between 70° to 80°C, but the absorption of the dye is very slow and the dye-bath is never exhausted. Consequently full shades are not obtained on wool even by this method.

It has been noticed, in the course of this investigation, that both the amino groups in 2:7-diaminophenanthraquinone reacts with aldehydes only when they are heated

together alone (*i.e.*, in the absence of any solvent). On the other hand in the presence of a solvent only one of the amino group reacts with aldehyde, even when there is an excess of the latter.

EXPERIMENTAL.

Phenanthraphenazine-2 : 7-bis-(1'-azo-2'-naphthol)—62 Grams of 2 : 7-diaminophenanthraphenazine, dissolved in 10 c.c. of concentrated hydrochloric acid (sp. gr. 1.15) and cooled to 0°C, was diazotised in the usual way, and the diazo solution added to an ice-cold solution of 0.6 grams of β -naphthol with 5 grams of caustic soda. The solution, which at once became violet, was stirred for one hour and left over-night. Next day the dye-stuff was precipitated by the addition of dilute hydrochloric acid. It was then filtered, washed and boiled under reflux to remove excess of β -naphthol. All attempts to crystallise it from various solvents were unsuccessful.

It does not melt up to 300°C; is slightly soluble in ether or alcohol, more soluble in acetic acid, acetone, pyridine or nitrobenzene. It dissolves in concentrated sulphuric acid with a reddish-violet colour, and dyes wool in reddish-violet shades from an acid-bath and cotton in pinkish shades from a neutral bath. (Found: N=13.52. $C_{40}H_{24}O_2N_8$ requires N=13.54 per cent.).

Phenanthraphenazine-2 : 7-bis-(1'-azo-2'-hydroxy-3'-naphthoic acid) was prepared from 2 : 7-diaminophenanthraphenazine (1 mol.) and 2'-hydroxy-3'-naphthoic acid (2 mols.) in the same way as the preceding compound.

It dyes wool in violet shades from an acid bath and cotton in light violet shades from a neutral bath. In its other properties it resembles the preceding compound (Found: N=12.26. $C_{42}H_{24}O_6N_7$ requires N=11.6 per cent.).

2-Amino-phenanthraquinone-7-(1'-azomethine-4'-dimethylamino-benzene) $(2)\text{NH}_2 \cdot \text{C}_{14}\text{H}_8\text{O}_2\text{N}(7) : \text{CH}(1') \cdot \text{C}_6\text{H}_4\text{N}(\text{Me})_2(4')$.—Separate solutions of 4 grams of 2:7-diaminophenanthraquinone and 3 grams of dimethyl-*para*-amino-benzal-dehyde in moderately strong hydrochloric acid, were mixed together and well-shaken, when the hydrochloride separated as a reddish precipitate. This was filtered, washed with water, then suspended in water and the free base liberated by the addition of ammonia. This separated from hot pyridine, on the addition of hot water, as shining, blue-black long needles, not melting below 300°C .

It is insoluble in ether or alcohol, and soluble in acetone, nitrobenzene or pyridine. It gives a yellowish-brown colour with concentrated sulphuric acid and dyes wool in bottle-green shades from acetic acid bath. (Found: $\text{N}=11.66$. $\text{C}_{23}\text{H}_{19}\text{O}_2\text{N}_3$ requires $\text{N}=11.38$ per cent.).

2-Amino-phenanthraquinone-7-(1'-azo-methine—2': 4'-dihydroxy-benzene) was obtained as black needles from 2:7-diamino-phenanthraquinone (1 mol.) and resorcylic aldehyde (1 mol.) in the same way as, and possesses similar properties to, the preceding compound. (Found: $\text{N}=8.07$. $\text{C}_{21}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{N}=7.82$ per cent.).

The following five phenyl-azo-methines were prepared, in the same way, by heating the amino-quinone with excess of the aldehyde for half-an-hour under reflux. The crystals, coming out on cooling, were further purified by first washing with ether and then boiling with alcohol for some time. They form most beautiful and shining crystals, and possess similar properties. They are insoluble in ether or alcohol, but soluble in acetone, nitrobenzene or pyridine. They dissolve in strong sulphuric acid with a brown colour and dye wool in reddish-violet shades from acetic acid bath. They do not melt below 300°C .

Phenanthraquinone-2 : 7-bis-(1'-azo-methine-benzene), $C_{14}H_6O_2(N=CH-C_6H_5)_2$ —was obtained, as shining violet prisms, from 2 : 7-diaminophenanthraquinone (4 grams) and benzaldehyde (10 c.c.). (Found : $N=7.26$. $C_{28}H_{18}O_2N_2$ requires $N=6.76$ per cent.).

Phenanthraquinone-2 : 7-bis-(1'-azo-methine-4'-methyl-benzene), prepared from 2 : 7-diaminophenanthraquinone and *p*-tolyl-aldehyde, separated as brilliant needle-shaped crystals of coppery lustre. (Found : $N=6.75$. $C_{30}H_{22}O_2N_2$ requires $N=6.33$ per cent.).

Phenanthraquinone-2 : 7-bis-(azo-cinnamylidinemethine), obtained from 2 : 7-diaminophenanthraquinone and cinnamic aldehyde, crystallised in shining violet needles. (Found : $N=5.71$. $C_{32}H_{22}O_2N_2$ requires $N=6.008$ per cent.).

Phenanthraquinone-2 : 7-bis-(1'-azo-methine-4'-methoxy-benzene), prepared from the 2 : 7-diaminoquinone and anisic aldehyde, was obtained as shining reddish violet prisms. (Found : $N=6.00$. $C_{30}H_{22}O_4N_2$ requires $N=5.90$ per cent.).

Phenanthraquinone-2 : 7-bis-(1'-azo-methine-2'-hydroxy-benzene), was obtained, as brilliant, needle-shaped, shining scarlet crystals, by the condensation of the 2 : 7-diaminoquinone (4 grams) with salicylic aldehyde (10 c.c.). (Found : $N=6.14$. $C_{28}H_{18}O_4N_2$ requires $N=6.27$ per cent.).

2-Acetyl aminophenanthraquinone-7-(1'-azo-methine-2'-hydroxy-benzene).—The pinkish-white precipitate produced on adding 2 c.c. of salicylic aldehyde to a solution of 4 grams of 2 : 7-diaminophenanthraquinone in 20 c.c. of glacial acetic acid changed, on heating for a few minutes under reflux, to beautiful violet prismatic needle-shaped crystals. These were filtered, washed first with water and finally with ether. From a study of its properties it appears that the amino group in 2 position has been acetylated during the reaction.

It does not melt below 300°C . It is insoluble in ether, alcohol or acetone and soluble in pyridine. It is very sparingly soluble in cold concentrated hydrochloric acid, but moderately soluble in the boiling acid to a red solution which on dilution turns yellow, without any reprecipitation of the original substance. It is slightly soluble in caustic soda solution in the cold, but more soluble on warming. It dissolves in strong sulphuric acid with a blood-red colouration and dyes wool in violet shades from acetic acid bath. (Found: $\text{N}=6.95$. $\text{C}_{23}\text{H}_{18}\text{O}_4\text{N}_2$ requires $\text{N}=7.29$ per cent.).

2-Amino-phenanthraquinone-7-(1'-azo-methine-2'-hydroxy-benzene), separated as reddish-violet needles on allowing to stand for 24 hours a solution of .4 gram of 2:7-diamino-phenanthraquinone and 2 c.c. of salicylic aldehyde in 25 c.c. of absolute alcohol, and was further purified first by washing with ether and then by boiling for sometime with alcohol under reflux. It was found to contain a molecule of alcohol associated with it. It resembles the preceding compound in its properties (Found: $\text{N}=7.26$. $\text{C}_{21}\text{H}_{14}\text{O}_3\text{N}_2, \text{C}_2\text{H}_5\text{OH}$ requires $\text{N}=7.21$ per cent.).

Phenanthraquinone-4-(1-azo-methine-3'-nitro-benzene), was obtained from 4-aminophenanthraquinone (.4 grams) and *meta*-nitrobenzaldehyde (.3 grams) by boiling in glacial acetic acid (30 c.c.) for half-an-hour. The precipitate crystallised from pyridine in orange-red minute needles, not melting below 300°C . It dyes wool in chocolate shades from acetic acid bath. (Found: $\text{N}=8.18$. $\text{C}_{21}\text{H}_{12}\text{O}_4\text{N}_2$ requires $\text{N}=7.86$ per cent.).

The following compounds were prepared in a similar way, and resemble the preceding compound in properties.

Phenanthraquinone-2-(1'-azo-methine-3'-nitro-benzene) was obtained as brownish-black crystals from 2-amino-phenanthraquinone and *meta*-nitrobenzaldehyde (Found: $\text{N}=8.68$. $\text{C}_{21}\text{H}_{12}\text{O}_4\text{N}_2$ requires $\text{N}=7.86$ per cent.).

4-Amino-phenanthraquinone-5-(1'-azo-methine-3'-nitro-benzene), prepared from 4 : 5-diaminophenanthra-quinone (4 grams) and *meta*-nitrobenzaldehyde (6 grams), could not be obtained crystalline. It was purified from nitrobenzene and obtained as an amorphous violet powder, not melting below 300°C. (Found: N=11.58. $C_{21}H_{13}O_4N_3$ requires N=11.32 per cent.).

2-Amino-phenanthraquinone-7-(1'-azo-methine-3'-nitro-benzene), prepared from 2 : 7-diaminophenanthraquinone (4 grams) and *meta*-nitrobenzaldehyde (6 grams), crystallised out of nitrobenzene in violet needles. (Found: N=11.84. $C_{21}H_{13}O_4N_3$ requires N=11.32 per cent.).

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The Colour of Complex Diazoles

Part II

By

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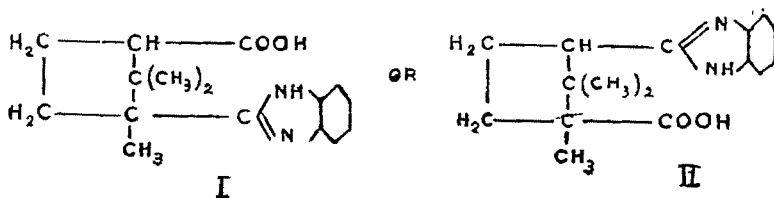
In a previous communication an attempt has been made by one of us (Chakravarti, this Journal, 1924, I, 19) to study the colour of compounds containing a condensed pyridine-iminazole ring system in their skeleton. It has already been pointed out that substances having a fused pyrrol-iminazole residue are coloured. The pyridine-iminazole derivatives prepared by Chakravarti (*loc. cit.*) as well as the compound, 1 : 2-*ortho*-benzoylene-acetyl-1 : 3-benziminazole obtained by Bistrzycki and Fässler (Helv. Chim. Acta., 1923, 6, 519) by the condensation of homophthalic anhydride with *ortho*-phenylene diamine were likewise found to be coloured. The present investigation was undertaken with a view to further elucidate the relation between the colour and constitution of the pyridine-iminazole systems. For this purpose camphoric anhydride was condensed severally with *ortho*-phenylene-, 1 : 3 : 4-*ortho*-tolylene-, and 1 : 2-naphthalene diamines. It was anticipated from the behaviour of analogous compounds that the diazoles so derived would all be coloured, but, contrary to this expectation it was found that they were all colourless.

A plausible explanation for the absence of colour in these diazoles appears to be that in camphoric anhydride a fully hydrogenised ring system is present, which may account for the hypsochromic effect on the iminazoles

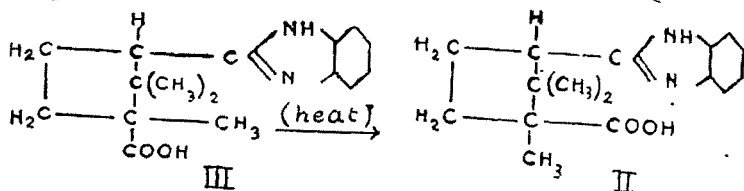
derived from it. But it seems to be an almost established fact that in the compounds of the fluorescein, eosin and rhodamine series derived from camphoric anhydride, the fully hydrogenised 'camphoryl' group has little or no deterrent effect on their colour. From an observation of the colour of these compounds as compared with those of the phthaleins, Sircar and Dutt (Trans. Chem. Soc., 1922, 121, 1283) conclude that the hydrogenised camphoryl residue seem to enhance the chromophoric properties of the dyestuffs obtained rather than cause any diminution in them. Singh, Rai and Lal (*ibid*, 1922, 121, 1421) from a comparative study of the absorption spectra of the camphoreins and the phthaleins state that the intensity of the colour of the former is only slightly less than that of the latter; whereas phenol-camphorein is admittedly more coloured than phenolphthalein. Evidently, the absence of colour in the camphor-diazoles which contain a piperidine-iminazole ring system cannot be explained by any of the experimental evidences so far obtained. It is, therefore, quite natural to assume that the condensed pyrrol-, pyridine-, and piperidine-iminazoles by themselves do not form the chromophores in the coloured complex diazoles. On the other hand, the colour may be due to the presence in the molecule of a kind of unsaturated linkages like the *ortho*- and *para*-quinonoid structures in benzenoid compounds which on being destroyed by hydrogenation as in the case of the camphor-iminazoles result in the production of colourless compounds. But this view of the structure of these diazoles requires further investigation and cannot be taken without qualification.

Camphoric anhydride condenses with *ortho*-phenylene diamine in alcoholic solution and furnishes a mixture of three phenylene-amidine-trimethyl-*cyclo*-pentane carboxylic acids with melting points 203°, 233°, and 240-42°.

The compound with m. p. 203° solidifies on further raising the temperature above this point and again melts at 242° . Their percentage composition is the same. These compounds are therefore isomeric. Camphoric anhydride might give rise to two isomeric amidine-carboxylic acids in the following manner:—



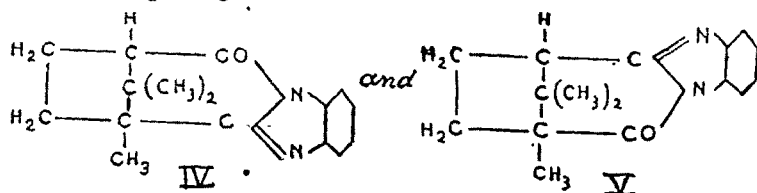
The acids melting at 233° and 242° are represented by either of the above configurations. What then, represents the third acid melting at 203° ? As the latter is transformed into the compound melting at 242° on heating it is evident that the isomerism exhibited in this case is similar to that observed in the case of the camphoric and *iso*-camphoric acids (*Cf.* Ber., 27, 2001, etc.), thus:—



As the physical properties, such as solubility in solvents, etc., of these acids differ very slightly from one another their separation from a mixture containing them and subsequent purification could only be accomplished after considerable difficulty.

On being heated with acetic anhydride each of the above acids loses a molecule of water and is converted into the corresponding diazoles which are found to be

colourless. The diazoles are, therefore, represented by the following diagrams:—



Camphoric anhydride on being similarly treated with 1 : 3 : 4-*ortho*-tolylene diamine yields a mixture of three acids. Two of them are represented by diagrams similar to (I) and (II) shown above, whereas the other differs from the rest by its possessing chloroform of crystallisation instead of alcohol or acetone which the former possess.* These acids also furnish the corresponding diazoles on treatment with acetic anhydride. 1 : 2-Naphthylene diamine and camphoric anhydride condense together in an analogous manner and yield a similar series of compounds.

The condensation of *ortho*-diamines with camphoric anhydride might give rise to several stereo-isomeric acids and the corresponding diazoles, of which only a few have actually been isolated and described. Unless a systematic study of these acids alone is undertaken, no definite formula can be attributed to any of the diazoles. As the

* These compounds as well as the diazoles derived from them have a strong tendency to combine with certain solvents like alcohol, acetone, benzene, toluene, etc., and they refuse to crystallise unless these solvents are present at least in small quantities. This has been determined in some cases by the direct estimation of their carbon and hydrogen contents. The products do not part with these solvents even on strong heating, whereby the compounds themselves are destroyed. On cautious heating the solvents are only partially removed. The difficulty the authors encountered in completely freeing the compounds from their solvents of crystallisation, led them to avoid solvents having tendency to enter into the compounds and crystallise them from light petroleum. Petrol ether was, however, found to be unsuitable as a crystallising medium for the crystallisation of the anhydrous diazoles in all cases and hence only a few of the latter have been described. The solvents entering into combination should more properly be termed solvent of constitution rather than that of crystallisation.

purpose of the present investigation was the study of the colour of these diazoles rather than a complete examination of the constitution of all the possible stereoisomeric acids and the corresponding diazoles, the authors thought it unnecessary at this stage to go into details to determine their spatial configurations, it being assumed that the colours of these compounds are in no way dependent on their stereoisomerism. The authors, however, intend to take up a polarimetric study of the acids as this may lead to interesting results.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with ortho-Phenylene Diamine. The Formation of Phenylene-amidine-trimethyl-cyclo-pentane Carboxylic Acids.—3.8 gms. of camphoric anhydride was mixed with 2.6 gms. of *ortho*-phenylene diamine and the mixture dissolved in about 120 c.c. of absolute alcohol. The mixture was heated under reflux for four to five hours and the alcohol distilled off. The pasty residue was washed repeatedly with hot toluene in which the unreacted anhydride and the diamine and also a small portion of the reaction products were soluble (a). The mass left behind was dissolved in a small quantity of absolute alcohol and poured into a large volume of water when a granular precipitate was obtained. This was washed repeatedly with anhydrous ether in which a portion dissolved (b) leaving behind a crystalline powdery mass of phenylene-amidine-trimethyl-cyclo-pentane carboxylic acid melting at 233°(I). (Found: C=70.39; H=7.11; N=10.21. $C_{16}H_{23}N_2O_3$ requires C=70.58; H=7.25; N=10.29 per cent.). The compound is completely soluble in alkaline carbonates and bicarbonates and is precipitated from solution in the form of a light amorphous powder on acidifying with dilute acetic or mineral acids. It is

exceedingly soluble in acetone, chloroform, methyl and ethyl alcohols but insoluble in ether, benzene and toluene.

The ethereal solution (b) was evaporated and the residual mass crystallised from methyl alcohol. This amidine carboxylic acid melts at 203° (III). On further heating it solidifies and melts again at 242° with decomposition (see below). This is an acid and resembles the previous compound in chemical and physical characteristics. (Found: $N=10.25$. $C_{18}H_{20}N_2O_2$ requires $N=10.29$ per cent.). The residue left after evaporation of the methyl alcoholic mother-liquor was treated with a solution of sodium carbonate when a small portion remained insoluble, which was crystallised from dilute alcohol, and melted at 132° . The toluene was distilled off from extract (a) and the residue washed with dilute sodium carbonate solution (c) when a further quantity of the product melting at 132° was obtained. This compound is identical with the diazole described below. The sodium carbonate solution (c) on being neutralised with dilute acetic acid yielded a precipitate of a phenylene-amidine-trimethyl-cyclo-pentane carboxylic acid, which was crystallised from alcohol. It melted at 238° to 242° * with decomposition (II). (Found $N=10.41$. $C_{18}H_{20}N_2O_2$ requires $N=10.20$ per cent.). That the acids (I) and (II) are different has been settled by a mixed melting point determination. In fact, the m. p. of an equivalent mixture of the two was considerably lower than that of either of the original substances. The diazole obtained from acid (II) was found to be identical with that from acid (III) (*vide infra*). The diazoles from (I) and (II) were distinctly different with m. p.'s 132° and 138°

* The meeting points of these acids were never so definite as represented above. The temperatures slightly vary according to the duration of heating owing to the formation of the corresponding diazoles which are all of lower melting points.

respectively. The mixed melting point of these two diazoles was also found to be much below their individual melting points.

When camphoric anhydride and *ortho*-phenylene diamine were fused together between 150° and 160° for half-an-hour, the major product was the acid melting at 242° together with a fairly large amount of diazole (*vide infra*); when, however, the condensation was carried on in alcoholic solution, the predominant portion was the acid with m. p. 233° . In both these reactions a small amount of the *ortho*-phenylene-diamine-camphorein is always formed which gives an intense red coloration in acid solution turning into yellow on adding alkalis. The compound was not further studied.

Diazole derived from compound (II).—The amidine carboxylic acid m. p. 233° was heated under reflux with excess of acetic anhydride for about two hours and the solution on cooling poured into a large volume of water and treated with excess of sodium carbonate. The semi-solid mass obtained was dissolved in a minimum quantity of alcohol and precipitated by water containing a little sodium carbonate, whereby a crystalline product melting at 132° was obtained. (Found: C=70.06; H=8.20; N=8.05. $C_{16}H_{18}N_2O$, $1\frac{1}{2}C_2H_5OH$ requires C=70.58; H=8.36; N=8.66 per cent.).

Diazole derived from Compound (III).—This diazole was obtained in a similar manner from the acid m. p. 203° and melted at 138° . (Found: N=8.59. $C_{16}H_{18}N_2O$, $1\frac{1}{2}C_2H_5OH$ requires N=8.66 per cent.). The diazole from compound II was prepared in an analogous manner and was found to melt at 138° and to be identical with that obtained from (III).

The *diazole* isolated from the products of fusion of the anhydride and the diamine was crystallised from

light petroleum and melted at 77° . (Found $N=11.22$. $C_{16}H_{18}N_2O$ requires $N=11.02$ per cent.).

The *diazole* derived from compound (I) m. p. 233° when extracted and purified with light petroleum instead of alcohol melted at 95° . (Found : $N=11.09$. $C_{16}H_{18}N_2O$ requires $N=11.02$ per cent.).

Condensation of Camphoric Anhydride with 1 : 3 : 4 :—ortho-Tolylene Diamine—The Formation of Tolylene-amidine-trimethyl-cyclo-pentane Carboxylic acids.—6 grams of the anhydride and 4 grams of the diamine were boiled together with 150 c.c. of absolute alcohol for 5 hours. The alcohol was distilled off and the residue extracted with hot toluene repeatedly (*d*). The final residue was dissolved in a minimum quantity of alcohol and precipitated by adding the solution to a large volume of water. The precipitate was dried, dissolved in acetone and treated with excess of ether. An acid slowly crystallised out on standing which was washed with ether and melted at $239-40^{\circ}$ (compare formula I). (Found : $C=65.00$; $N=6.32$. $C_{17}H_{22}N_2O_2$, $3(CH_3)_2CO$ requires $C=65.09$; $N=6.60$ per cent.). The mother-liquor on evaporation and treatment with acetone and ether for a second time gave a further product which was recrystallised from a mixture of chloroform and ether. This acid melts at $228-29^{\circ}$ and contains chloroform of crystallisation. (Found : $N=6.16$. $C_{17}H_{22}N_2O_2$, $1\frac{1}{2}CHCl_3$ requires $N=6.02$ per cent.).

The toluene from extract (*d*) was distilled off and the residue treated with dilute sodium carbonate solution. A portion remained insoluble which was extracted with petroleum ether; the portion insoluble in the latter is supposed to be the tolylene-diamine-camphorein because like its phenylene analogue it gave characteristic colour reactions with acids and alkalis. The petroleum solution was evaporated, the viscous residue dissolved in

alcohol and purified by pouring into a large volume of water. This was found to be identical with the diazole melting at 97° . The portion of the extract (d) which dissolved in sodium carbonate solution was neutralised with dilute acetic acid and the precipitate crystallised from 50—60 % alcohol. The crystals melt at $250-52^{\circ}$ (compare formula II). (Found: $N=6.49$. $C_{17}H_{22}N_2O_2$, $3C_2H_5OH$ requires $N=6.60$ per cent.).

Diazoles derived from Toluene-amidine-trimethyl-cyclopentane-carboxylic acids.—Each of the acids with m. p. $239-40^{\circ}$ and $250-52^{\circ}$ were boiled with excess of acetic anhydride and the diazoles were isolated in a manner exactly similar to the phenylene compounds (*vide supra*). They were colourless and melted at 93° and 97° respectively and contained alcohol of crystallisation. They lose alcohol partially on heating and even in a vacuum desiccator. They were therefore air dried and analysed. (Found: $N=6.62, 6.70$. $C_{17}H_{20}N_2O$, $3C_3H_5OH$ requires $N=6.89$ per cent.).

Condensation of Camphoric Anhydride with 1:2-Naphthylene Diamine. The Formation of Naphthylene amidine-trimethyl-cyclopentane Carboxylic Acids.—Equimolecular quantities of the anhydride and the diamine were boiled together in absolute alcohol for 5 hours. The alcohol was distilled off, the residue washed with hot toluene, dissolved in alcohol and precipitated by water. The precipitate was washed thoroughly with water and dissolved in dilute sodium carbonate solution. Two different colourless amidine carboxylic acids were obtained by fractional precipitation of the solution with acids. They were further purified by solution in alcohol and precipitation with water. One acid (compare formula I) had the melting point $180-82^{\circ}$ (Found: $N=8.63$. $C_{20}H_{23}N_2O_2$ requires $N=8.69$ per cent.). The other acid melted at 235° with decomposition. (Found:

$N=7.06$ ($C_{20}H_{22}N_2O_2$, $1\frac{1}{2}C_2H_5OH$ requires $N=7.16$ per cent.).

The Diazole.—The acid (with m.p. $180-82^\circ$) was as before treated with acetic anhydride and the diazole was obtained like its previous analogues and melted at $80-82^\circ$. (Found: $N=8.09$. $C_{20}H_{20}N_2O$, C_2H_5OH requires $N=8.00$ per cent.).

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